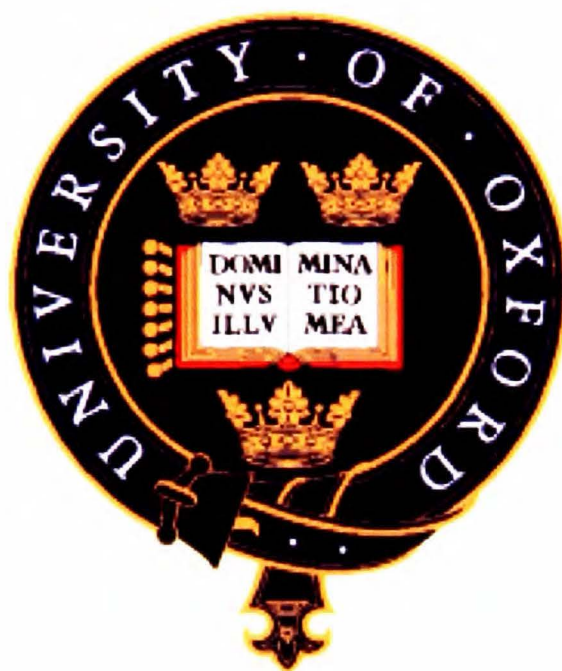


FABRICATION AND PROPERTIES OF OXIDE NANOCOMPOSITES CONTAINING UNIFORMLY DISPERSED SECOND PHASES

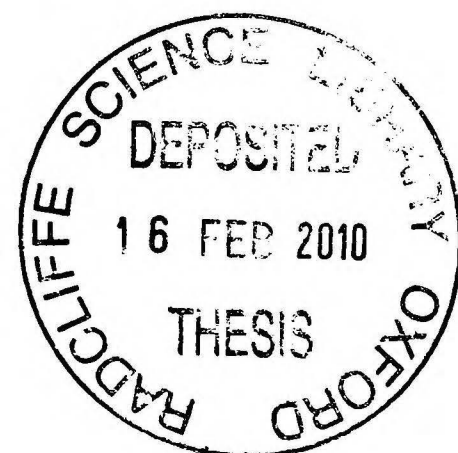
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**A Thesis submitted for the degree of Doctor of Philosophy
at the University of Oxford**

Michaelmas Term, 2009



Fabrication and Properties of Oxide Nanocomposites containing Uniformly Dispersed Second Phases

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Abstract

The present research addresses some of the major problems pertaining to two different types of ceramic nanocomposite; viz. particulate reinforced polycrystalline alumina-based nanocomposites and multiwalled carbon nanotube (MWCNT) reinforced aluminoborosilicate glass/ceramic (ABS) nanocomposites. With respect to the former, a novel and economical processing route based upon solid solution-precipitation technique is explored. Dense and homogeneous solid solutions of 10 wt.% Fe_2O_3 in Al_2O_3 were produced by pressureless sintering at 1450°C in air. Aging of the solid solutions in a reducing atmosphere at temperatures in the range 1250°C - 1550°C for different durations (up to 50 h) resulted in the precipitation of FeAl_2O_4 as second phase particles throughout the bulk of the samples. The optimum aging schedules resulted in a final microstructure comprising nanosized (~ 100 nm) intragranular FeAl_2O_4 particles, along with coarser micro-sized particles along the matrix grain boundaries and triple point corners. The hybrid nano/micro composites possessed improved fracture toughness (by $\sim 40\%$), flexural strength (by $\sim 50\%$) and abrasive wear resistance (by a factor of ~ 2.5) with respect to monolithic Al_2O_3 .

With respect to the ABS - MWCNT nanocomposites, we report here the ability to develop dense nanocomposites, containing uniformly dispersed nanotubes up to a content of 10 wt.%, by an ultrasonication-assisted sol-gel technique followed by hot pressing. The optimised ABS - 10 wt.% MWCNT nanocomposite possessed nearly double the strength, and a fracture toughness improvement of $\sim 150\%$ with respect to the unreinforced ABS. The carbon nanotubes have been observed to bridge crack openings of the order of ~ 100 nm which provides the major contribution towards the improvement in fracture toughness. The nanocomposites, showed an electrical percolation threshold of between 2.5 to 5 wt.% MWCNT and possessed significantly higher electrical conductivities (by a factor of 10^6) with respect to the unreinforced ABS glass/ceramic. Furthermore, 40% improvement in thermal conductivity ($\sim 1.8 \text{ W m}^{-1} \text{ K}^{-1}$) over that of unreinforced ABS glass/ceramic was recorded with ABS - 15 wt.% MWCNT nanocomposite.

Preface

The work presented in this thesis was carried out by the author in the Department of Materials, University of Oxford, under the supervision of Dr. Richard I. Todd. The work in this thesis is original and no part of this thesis has previously been submitted for a degree at this or other University.

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October, 2009

Amartya
Oxford University

Dedicated To,

“My Parents”

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Chapter 1

INTRODUCTION

Materials possessing structural units with characteristic length scales less than hundred nanometers in any dimension are placed under the generic heading of ‘Nanostructured Materials’. This length scale could refer to particle diameter, fibre diameter, grain size, layer thickness or even the width of a conducting line on an electronic chip. Based on their dimensions, nanostructured materials are classified as zero-dimensional (nanosized powders), one-dimensional (nanocrystalline multilayer or carbon nanotubes), two-dimensional (filamentary rods of nanoscale thickness) and three dimensional (bulk materials with at least one nanocrystalline phase) [1,2]. Realization of the fact that nanostructured materials have the potential to exhibit superior or novel properties (physical, chemical, mechanical, functional) with respect to their conventional counterparts has triggered significant research activity on their development and characterization. Extensive research efforts over the last few decades have been quite successful in devising some means for overcoming the primary challenges involved in the processing of various nanomaterials, in developing a preliminary understanding of the structure-property correlation of nanomaterials and in recognizing their potential for several demanding structural and advanced technological applications.

1.1. Ceramic Nanocomposites

In the light of some pioneering reports indicating the possibility of achieving considerable improvements in physical, mechanical and tribological properties by nanocomposite design [1-9], the last few years have witnessed an upsurge of interest towards the development and characterization of bulk ceramic-based nanocomposites.

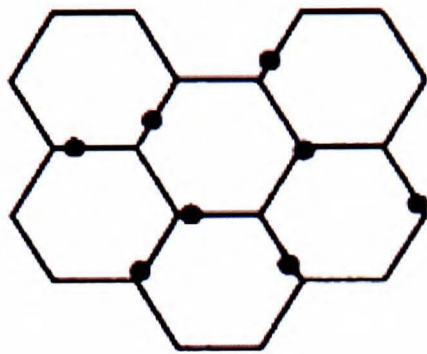
Ceramic nanocomposites can be broadly classified into two categories; viz. nanoparticulate reinforced composites and nano-fibre reinforced composites.

1.1.1. Particulate Ceramic Nanocomposites

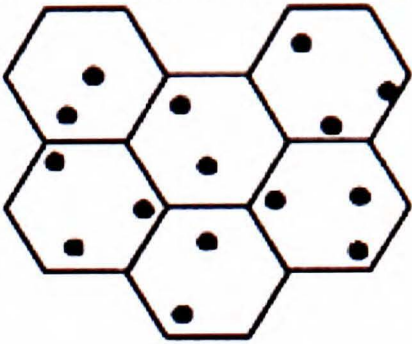
Ceramic nanocomposites containing nanosized particles or grains as secondary phases were first developed in Japan by K. Niihara who claimed that ceramic materials with excellent mechanical properties can be obtained through nanocomposite design [3]. Based on the distribution of the second phase particles with respect to the matrix grains, the particulate ceramic nanocomposites can be further classified into the following microstructural classes [3];

- (a) Intergranular nanocomposites, where the nanosized reinforcements are present at the grain boundaries and triple junctions of the matrix grains;
- (b) Intragranular nanocomposites, which contain the nanoscaled reinforcements within the matrix grains;
- (c) Inter/Intragranular nanocomposites, where the nanosized reinforcements are present at the grain boundaries and triple junctions as well as within the matrix grains;
- (d) Nano/Nanocomposites, in which case both the matrix and the reinforcement particulates are in the nanosized range;
- (e) Nano/micro-composite encompasses another slightly different nanocomposite microstructural design, which is characterized by the dispersion of micron sized particulates in nanosized matrix [1,10]. A schematic representation of the various model nanocomposite structures is shown in Fig. 1.1.

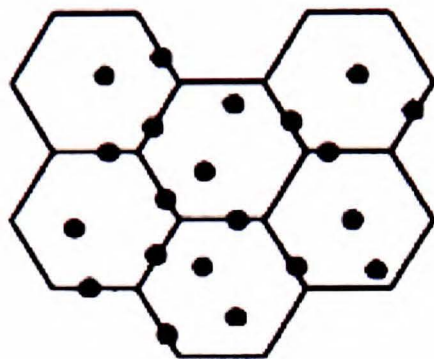
(a) Intergranular nanocomposite



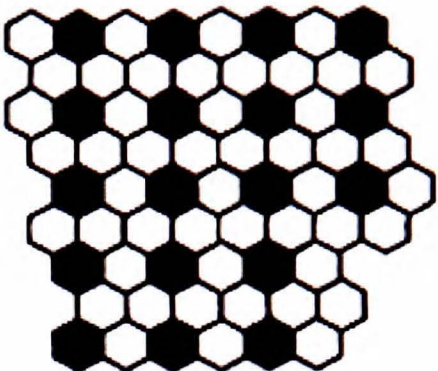
(b) Intragranular nanocomposite



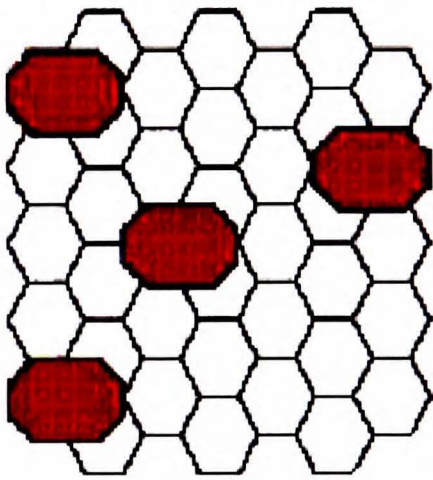
(c) Inter/intragranular nanocomposite



(d) Nano/nanocomposite



(e) Nano/micron composite



100 nm

Fig. 1.1. Schematic representation of the classification of particulate reinforced ceramic nanocomposites based on relative sizes and distribution of the microstructural phases [1,3,10].

1.1.2. Ceramic Composites Reinforced with Nano-Fibres

Nanocomposites based on crystalline ceramics or glasses can also be developed by using fibres possessing diameters of less than ~ 100 nm and concomitantly high aspect ratios as second phase reinforcements. Such nanocomposite design has been realized mainly after the discovery of carbon nanotubes by Iijima [11] in the same year (1991) and the same country (Japan) as particulate nanocomposites were designed by Niihara [3]. Basically carbon nanotubes (CNTs) are tubular derivatives of fullerenes (cage like structures of carbon atoms) which consist of graphene cylinders generally closed at both ends with the caps containing pentagonal rings. Ever since their discovery the CNTs are regarded as the ultimate fibre by virtue of their exceptional mechanical and physical properties, which are superior to most other materials. Coupled with the exceptional properties, CNTs possess very large aspect ratios (often > 1000) which make them potential candidates for use as nano-fibre reinforcements in composites [7-9,11-15].

Though no recognized generic microstructural classification exists for nano-fibre reinforced ceramic composites, as opposed to particulate nanocomposites, different microstructural developments are possible for CNT reinforced ceramic composites (see Fig. 1.2). Such nanocomposites can be developed by using either single walled carbon nanotubes (SWCNTs) or multiwalled carbon nanotubes (MWCNTs) as second phase reinforcements. Basically, MWCNTs consist of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow core with interlayer separation of ~ 0.34 nm, as in graphite. The diameters of SWCNTs normally have a narrow size distribution (1-3 nm); whilst the diameters of MWCNTs can be up to 100 nm [11-15]. The nanocomposites can be fabricated using either directionally oriented or randomly oriented CNTs. Fig. 1.2a and b present schematic

representations of such directionally oriented CNT reinforced ceramic nanocomposites. In the bulk nanocomposites containing randomly oriented CNTs, the microstructural development differs with respect to the ceramic matrix, whether polycrystalline or glass. For polycrystalline matrices, it is more frequently observed that the nanotubes exist as bundles along the grain boundaries [16-18] (Fig. 1.2c), although microstructural developments characterized by CNTs penetrating the matrix grains have also been achieved [19] (Fig. 1.2d). For glasses, which are devoid of grains/grain boundaries it is possible to develop glass - CNT nanocomposites with CNTs dispersed homogeneously throughout the bulk [20] (Fig. 1.2e). However, it is observed that CNTs tend to form agglomerates even in such nanocomposites (Fig. 1.2f) [21,22].

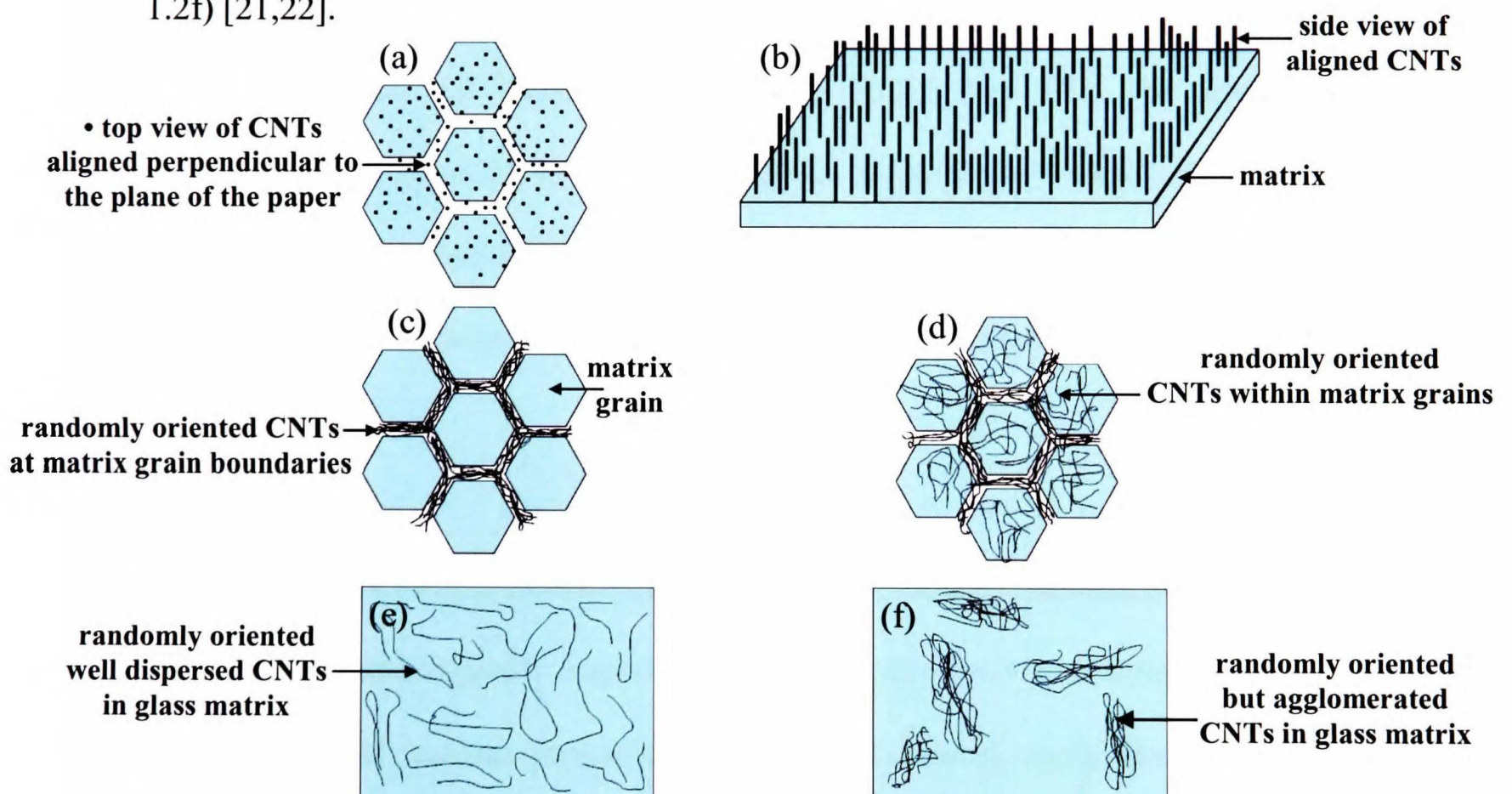


Fig. 1.2. Schematic representation of the different microstructural developments possible for CNT reinforced ceramic nanocomposites. (a) Top view and (b) side view of directionally oriented (aligned) CNT - ceramic nanocomposites; randomly oriented CNT - polycrystalline ceramic nanocomposites containing (c) CNTs at matrix grain boundaries only and (b) CNTs also within matrix grains; randomly oriented glass - CNT nanocomposites containing (e) well dispersed nanotubes and (f) nanotube agglomerates.

1.2. Advantages of Ceramic Nanocomposites

Despite possessing superior refractoriness, hardness, elastic modulus, creep resistance, wear resistance and inertness towards aggressive environments, with respect to the other materials classes, the inherent brittleness of ceramic-based materials severely limits their use in demanding structural applications. Against this backdrop, it has been reported that reinforcement of the ceramic matrix by nanosized particles (particulate ceramic nanocomposites) or nano-fibres (fibre reinforced ceramic nanocomposites) may lead to considerable improvement in the room temperature as well as high temperature mechanical properties, in particular the fracture toughness, strength and creep resistance [1,3-8,23-29]. Also, the presence of nanosized particles as secondary phases has been reported to result in considerable improvements in the tribological properties [1,5,6,29,31-43]. Furthermore, the reinforcement of ceramics by some nano-fibres, in particular carbon nanotubes, may also lead to the improvement of electrical and thermal conductivity, as well as thermal shock resistance for these insulating inorganic material classes [44-49].

1.2.1. Beneficial Effects of Nanosized Particulate Reinforcements in Alumina

One of the technologically important structural polycrystalline ceramics, which is widely used for various structural and wear resistance applications, is alumina (Al_2O_3). Monolithic Al_2O_3 possesses a very high melting point ($\sim 2100^\circ\text{C}$), Young's modulus (~ 400 GPa) and hardness (~ 20 GPa), along with considerable wear resistance. However, its inferior fracture toughness ($\sim 3 \text{ MPa m}^{1/2}$) and modest flexural strength (~ 350 MPa) limit its structural applications considerably. This issue was initially addressed by Niihara in his pioneering paper concerning the

development of particulate ceramic nanocomposites [3]. A significant improvement of strength and fracture toughness, along with considerable improvement in hardness, was reportedly achieved by the incorporation of nanosized SiC particles (~ 5 vol.%). Such report triggered significant research activities concerning the development of Al₂O₃-based nanocomposites containing various nanosized second phase particles.

Among the various properties, which render structural ceramics useful in high-tech applications, wear resistance stands out to be one of the most important. The field of tribological applications, which can be broadly defined as applications involving interacting surfaces in relative motion, probably encompasses the major applications of ceramics as structural parts at ambient as well as elevated temperature. It must be mentioned here that 'Wear' is the removal of materials from contacting surfaces in relative motion. Typically wear is quantified with wear rate, which is defined as the volume of material worn or depth of material removed per unit time at constant load.

In this light, one of the most significant benefits of the development of ceramic-based nanomaterials has been the outstanding improvement in the wear resistance. Ever since the realization of the possibility of property improvements via nanoceramics or ceramic nanocomposites formation, extensive research has been directed towards investigating the tribological properties of various particulate reinforced ceramic nanocomposites. The results of nearly all such research activities proclaim that the tribological properties of nanoceramics and ceramic nanocomposites, particularly in the severe wear regime, are superior to those of conventional ceramics [1,6,29,31-43].

It can be noted that such a unified consensus on the improvement of wear resistance is in contrast to the considerable debate over the improvement of mechanical properties for particulate reinforced ceramic nanocomposites. Hence, research results concerning

the wear resistance of nanostructured ceramics promise to enhance the commercial applicability of structural ceramics.

1.2.2. Potential Advantages of Reinforcing Borosilicate Glass with CNT

Among various ceramic glasses, borosilicate glass, by virtue of its excellent corrosion resistance, moderate thermal shock resistance and low thermal expansion co-efficient, is extensively used in various important technological applications, ranging from laboratory wares to use in electronic industries [21,22,50-54]. On one hand, its superior resistance towards attack by various chemicals and corrosive environments makes it suitable for use in chemical industries, and on the other hand its low thermal expansion co-efficient of $\sim 3 \times 10^{-6} / ^\circ\text{C}$, which is similar to that of Si, makes it a potential candidate for use as substrates for Si chips [50,51]. However, the inferior mechanical properties, in particular brittleness, of borosilicate glass considerably hinder its application as substrate materials [51,54], along with other structural applications. Furthermore, the insulating nature of borosilicate glass is also detrimental towards its extensive use in such applications. Against this backdrop, research efforts have been devoted towards reinforcement of borosilicate glass with carbon fibres, leading to modest improvements of the mechanical properties as well as thermal conductivities [55,56].

Considering that carbon nanotubes, which possess exceptional mechanical properties, thermal and electrical conductivities and high aspect ratios as compared to any other nano-fibres, are probably one of the most potent fibre reinforcements, over the last decade research activities have been devoted towards developing CNT reinforced ceramic-based nanocomposites [7,8,12-22,24,44-49]. Although, as with particulate

reinforced ceramic nanocomposites, there has been considerable variation in the published results, the strengthening and toughening of polycrystalline ceramics and glasses have been regularly achieved on reinforcement with CNTs [7,8,12-15,19,20,57-61]. Furthermore, a few reports are also available which demonstrate that such ceramic - CNT nanocomposites can possess improved thermal and electrical conductivities [22,44-49]. In this light, recently a research group at Imperial College, London tried for the first time to develop borosilicate glass - MWCNT nanocomposites [21,22] and reported that considerable improvement in the electrical conductivity could be achieved for the nanocomposites.

1.3. Problems Associated with Ceramic Nanocomposites

Though the emergence of ceramic nanocomposites is promising from the view point of demanding technological applications, challenges involved in their successful processing stand out to be one of the major bottlenecks towards their commercial application. In general terms, most investigated bulk ceramic nanocomposites are made via powder metallurgical routes, which involve mixing of nanosized second phase powders or nano-fibres with the matrix powders, followed by sintering. In such a route, the difficulties in processing stem right from the initial nano-powder/nano-fibre preparation stage to the development of dense composites containing well dispersed nanosized particles or fibres.

1.3.1. Problems Specific to Particulate Reinforced Ceramic Nanocomposites

For particulate reinforced nanocomposites the major processing challenges can be broadly grouped into four categories, viz. synthesis of nanosized starting powders, prevention of agglomeration during powder handling, attaining near theoretical densification at moderate sintering temperatures and restriction of grain growth/particle coarsening beyond the nanosized regime during sintering via conventional sintering techniques [1,2-6,29]. From a commercial point of view the production of nanosized starting powders usually incurs greater expenditure as compared to conventional ceramic powders. Furthermore from the sintering point of view, in most cases it becomes imperative to use hot pressing or even advanced techniques such as spark plasma sintering (SPS) for developing dense bulk ceramic nanocomposites [1,2-4,6,10,25,29,31-34]. Such techniques possess serious drawbacks with respect to mass scale commercial production in the sense that, as well as being very expensive, they are not suitable for continuous batch production and severely limit the shape and size and dimensions of the components that can be produced. In this regard, continued research activities aim at overcoming the challenges involved in developing ceramic-based nanomaterials using cost effective processing routes.

Additionally, most of the developmental research to date on particulate nanoceramic composites has been focused on systems comprising at least one non-oxide phase [1,2-6,10,25,39,31-34,62]. Though such materials possess superior properties [1], the practical applications of such nanocomposites at high temperatures in air may lead to problems related to oxidation of the non oxide phases. Hence, in order to stimulate commercial application of ceramic matrix nanocomposites, it is imperative to develop ceramic nanocomposites consisting of only oxide phases that can be produced using

cheaper and more versatile processing routes, which are suitable for mass scale commercial production.

1.3.2. Problems Specific to Ceramic - CNT nanocomposites

The major problem associated with the CNT reinforced nanocomposites is the prevention of CNT agglomeration during bulk nanocomposite formation. Due to the extremely high aspect ratio, CNTs are vulnerable to agglomeration [7,8,12,21,22]. Furthermore, such problem is often exacerbated if ball milling is used for mixing the nanotubes with the matrix powders [20]. Such agglomeration results in the creation of defects and concomitantly the deterioration of the material properties. Additionally, the presence of CNTs in composites hinders densification severely which raises the sintering temperature required to obtain dense ceramic nanocomposites. High sintering temperature, as well as highly reactive processing environments, is detrimental since it also results in damage to the nanotubes [20,63]. On a different note, the CNT/matrix interface characteristics are also critical with respect to the nanocomposite properties and often the beneficial effects of CNT reinforcements are not realized due to either extremely weak or extremely strong bonding at the CNT/matrix interface [7,8,12,15].

Hence, the critical factors with respect to developing CNT reinforced composites possessing improved mechanical properties lie in (a) achieving homogeneous dispersions of the reinforcing CNTs in the parent matrix, (b) optimum bonding at the CNT/matrix interface, and (c) avoiding damage to the CNTs by using a lower (< 1000°C) sintering temperature.

1.4. Structure of the Thesis

The present thesis is concerned with the development and characterization of the two different kinds of ceramic nanocomposite, viz. oxide particle reinforced Al_2O_3 -based nanocomposites and CNT reinforced aluminoborosilicate glass ceramic (ABS) nanocomposites. Broadly this research aims to solve problems related to processing for both the nanocomposite classes and tries to investigate and critically understand the effects of the nanosized reinforcements on the mechanical properties. Furthermore, in the light of some specific potential applications for the two different nanocomposites, that is tribological applications for the Al_2O_3 -based particulate nanocomposites and application as substrate material in electronic chips for the CNT reinforced ABS nanocomposites, this work also investigates the wear resistance of the Al_2O_3 -based particulate nanocomposites and the electrical and thermal properties of the ABS - CNT nanocomposites.

- Following this introduction about the different ceramic nanocomposites, a comprehensive review of the present literature base is presented in chapter 2, which discusses the problems associated with the processing of nanocomposites, highlights the various approaches adapted to date to solve such problems and throws light on the structure-property correlations of particulate reinforced Al_2O_3 -based nanocomposites and CNT reinforced ceramic polycrystals/glasses based nanocomposites. Such detailed discussion on the outstanding issues concerned with ceramic nanocomposites leads to the purpose and aims of the present research.

- Details about the experimental procedures that were used for the present investigations involving both the nanocomposites are mentioned in the following chapter (chapter 3).

The next four chapters (chapters 4 to 7) are concerned with the results and discussions based on the present research investigations.

- More precisely, chapter 4 describes the phase and microstructural developments obtained while trying to develop particulate reinforced Al_2O_3 -based nanocomposites via the currently investigated novel solid state precipitation technique. Following the discussion on the processing and microstructure of the nanocomposites, results concerning the mechanical properties (mainly hardness, fracture toughness and flexural strength) of some of the Al_2O_3 -based nanocomposites developed under the optimum conditions are presented and discussed in correlation with the microstructural developments.
- Considering that tribological applications encompass one of the major fields of applications for structural ceramics and that particulate nanocomposites possess superior tribological properties with respect to conventional ceramics/composites, results based on abrasive wear tests of the Al_2O_3 -based particulate nanocomposites are presented in chapter 5. Understanding the interplay between the microstructural developments, composition, mechanical properties and the results obtained from the wear tests allow further

optimization of the processing conditions to develop high performance particulate reinforced Al_2O_3 -based nanocomposites.

- Chapter 6 presents the phase and microstructural developments achieved during the development of dense MWCNT reinforced ABS nanocomposites containing well dispersed MWCNTs at contents greater than 5 wt.% using the recently developed sol-gel based route [20]. Following this, results based on the investigation of different mechanical properties (mainly hardness, elastic modulus, fracture toughness and flexural strength) of the nanocomposites are presented. The results have been critically analysed to understand the effects of MWCNT reinforcements on the mechanical behaviour.
- With regard to the potential applications of borosilicate glass in electronic industries, which demand improved electrical and thermal conductivities in addition to mechanical strength, the electrical and thermal properties of the BSG - CNT nanocomposites are presented in chapter 7. Such results are analysed in the light of their variation with the CNT contents.
- Finally, the thesis concludes with chapter 8, which summarizes the notable achievements of the present work, along with a brief mention of some of the unresolved issues and the scope for future research on such bulk ceramic-based nanocomposites.

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Chapter 2

LITERATURE
REVIEW

2.1. Challenges Involved in the Development of Ceramic Nanocomposites

Research investigations over nearly a couple of decades have demonstrated the superiority of ceramic nanocomposites over their conventional counterparts, in terms of material properties and potentials for use in demanding applications [1-6]. However, to date ceramic nanocomposites have not been able to penetrate the commercial market. The major hindrance arises from the technical challenges and expenditure involved in the successful processing of such materials. As a result, one of the major focuses in the research on bulk ceramic nanocomposites encompasses processing related challenges for the different types of nanocomposites. The following sections present a detailed review of such problems, along with various approaches that have been and need to be adopted to overcome the respective challenges.

2.1.1. Processing Challenges Related to the Properties of Nanopowders and Nanotubes

Certain typical properties possessed by nanosized ceramic powders and carbon nanotubes pose considerable challenges with regard to handling and subsequent processing into bulk ceramic nanocomposites. To be precise, although the ultra fine dimensions and concomitant accrued interfacial areas of the nano-reinforcements result in improved properties of the bulk nanocomposites, such ultra fine dimensions are often the major sources of the difficulties encountered during processing [1-25].

2.1.1.1. Dispersion and Compaction of Nanosized Powders

One of the most significant problems, which is directly related to the higher specific surface area of the nanosized starting powders, is that of agglomeration [1,2,6]. The large specific surface area of the ceramic nanoparticles provides a strong driving force for agglomeration. A schematic representation (Fig. 2.1a), along with typical TEM micrographs of agglomerated nanoceramic powders synthesized via High Energy Ball Milling (HEBM) (Fig. 2.1b) and sol-gel (Fig. 2.1c) techniques is presented in Fig. 2.1 [2,10,11]. Note the presence of considerably larger inter-agglomerate pores, as compared to the inter-crystallite pores. In the case of agglomerated powders, agglomerate sizes and hence the larger inter-agglomerate pores dominate the densification behaviour resulting in slower overall densification rates.

One of the techniques used for preventing agglomeration is to introduce surface charges on the powder particles in suspension, leading to electrostatic repulsion among them [1,2,12]. Powder particles in suspension may also be dispersed by the use of certain surfactants, which are generally organic molecules consisting of long chains providing steric barrier to agglomeration. Although the use of appropriate surfactants has proved to be beneficial in reducing the degree of agglomeration, the ultra-fine dimensions of the nanopowders implicate the use of much smaller organic molecules than those used conventionally so that their lengths do not exceed the nanoparticles' diameters [1,2,13]. Since there is a tendency for the powders to agglomerate during drying of aqueous suspensions, adoption of specific drying techniques is critical with regard to control of net agglomeration. In this regard, freeze drying [1,2,5], in which the aqueous suspension is frozen for minimizing any molecular motion, prior to removal of the ice by sublimation, is frequently used to 'dry' aqueous slurries of ceramic nanopowders [1,2,14]. Another technique, which avoids agglomeration

during the drying step, is colloidal processing of slurries. One such process called slip casting is often used to produce green compacts of nanopowders with densities even better than those obtained by dry forming of conventional powders [7,16-18]. Also, replacement of water by organic solvents prior to drying, or using organic solvents as the dispersing media [1,2,15], is often employed to avoid agglomerate formation. Many processes and materials also require additional dispersion and physical disintegration of the remaining agglomerates of the as synthesized powders via centrifugation, ultrasonication and ball milling.

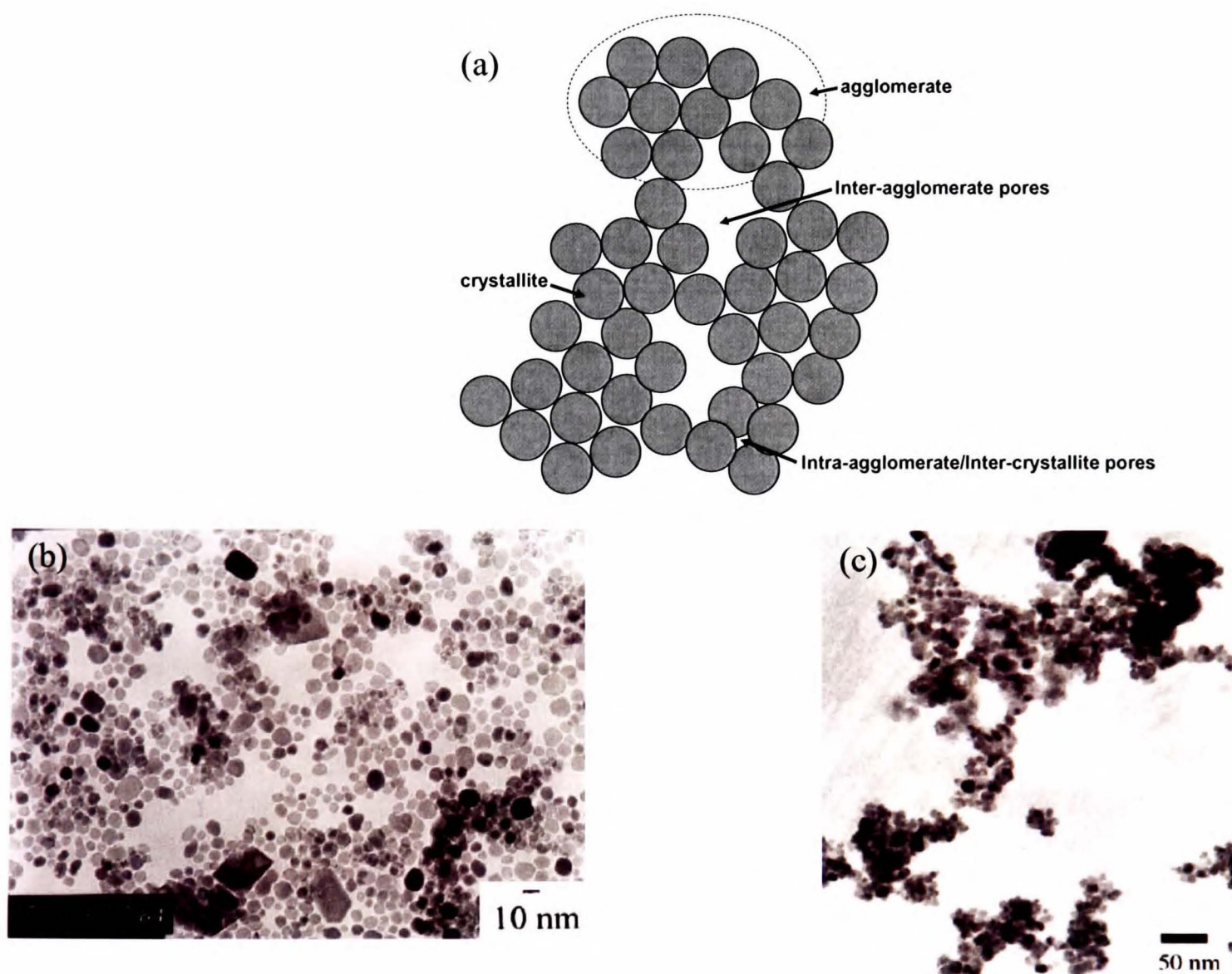


Fig. 2.1. (a) A schematic representation of nanoceramic powders, which illustrates the nature of particle agglomeration, an inherent problem related to nanopowders; (b) TEM image showing TiB₂-TiC nanocomposite powders, fabricated by HEBM [10]; (c) TEM micrograph of TiO₂ (anatase) nanopowders, synthesized via sol-gel method [11].

One of the preliminary processing steps involves the formation of green compacts with densities of around 60% of theoretical densities. However, using the pressures (~200 MPa) generally applied for making green compacts of conventional micron sized powders, it has been found to be difficult to fabricate green compacts of similar green densities from nanosized starting powders [1,2,7-9]. The reason lies in the enhanced surface area of the ultra fine powders, which leads to the total number of interparticle contacts becoming increasingly larger, as the powder particle sizes become progressively finer, resulting in an augmentation of the frictional resistance to the applied pressure during compaction [8]. However, another disadvantage arising from the application of too high a pressure is the possibility of introducing cracks and other defects into the green compacts.

2.1.1.2. Problems Related to Agglomeration and Purity of Carbon Nanotubes

The major hindrance towards successful development of ceramic-based composites reinforced with carbon nanotubes is the propensity of the nanotubes to become agglomerated. The high aspect ratios, strong Van der Waals forces between tubes and the flexibility of CNTs lead to physical entanglement. It has been observed that CNTs always tend to aggregate to form bundles or ropes and such agglomerates in nanocomposites hinder densification during sintering, lead to the creation of structural defects and also result in a reduction of the load carrying efficiency between the reinforcing phase and the matrix [19-25]. Fig. 2.2 presents an SEM image of agglomerated MWCNT produced by CVD technique.

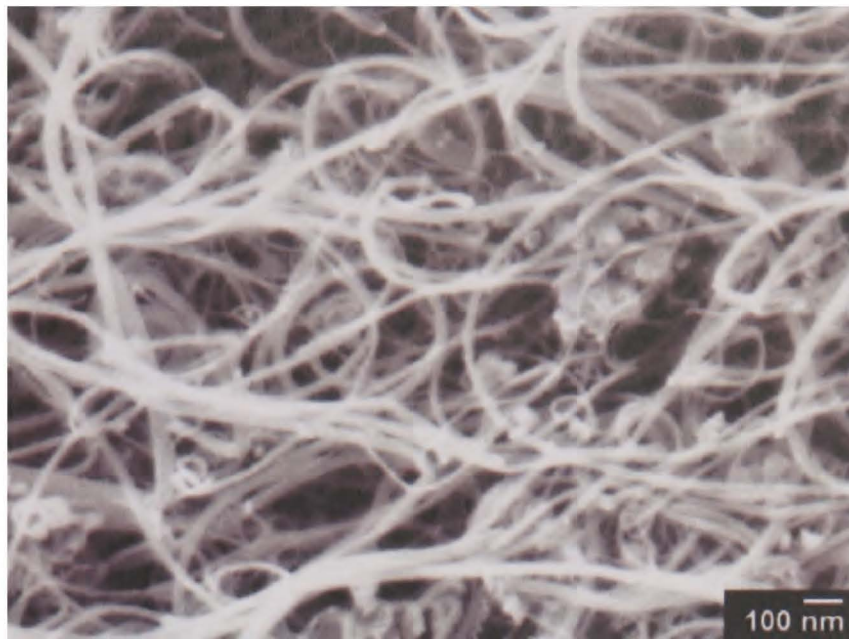


Fig. 2.2. SEM micrograph showing tangled, spaghetti-like carbon nanotubes produced via conventional CVD technique [20].

Hence the ability to disperse CNTs, and especially to mono-disperse them, is a critical factor which determines the successful processing and concomitantly the properties of the CNT reinforced nanocomposites. Recent research efforts have concentrated on developing effective means to disperse CNTs [26], while at the same time preserving their structural integrity and maintaining their length [27]. The strategies used for dispersing CNTs include a) using π - π induced interactions via physical adsorption of π -aromatic compounds in solvents [28]; b) making other non-covalent (Van der Waals, physical adsorption) bonding induced barriers to agglomeration, for instance, wrapping the CNTs with surfactants and polymers [28,29] or by using charged nanoparticles (such as ZrO_2) [30] and c) inducing covalently bonded side wall functionalization of CNTs. Such chemical modification of the CNT side walls by forming covalent bonds between the CNTs and different functional groups, such as aliphatic amines, carboxylates, esters etc. [27,31,32] can greatly improve the dispersion. However, it must be noted here that functionalization can induce damages along the outer walls of the CNTs [19-21,29-31]. Ultrasonic treatment also assists in keeping the CNTs dispersed in suspensions containing high concentrations of CNTs.

However, vigorous ultrasonication can cause damage and shortening of nanotubes [33]. An additional problem encountered during development of CNT containing nanocomposites is that if the different functional groups and adsorbates for dispersing nanotubes are not compatible with the matrix precursors, the dispersion tends to get destabilized once incorporated in the matrix precursors and often undesirable residues are left in the nanocomposites [22].

Another problem associated with the nanotubes is that usually they contain impurities such as metal catalyst particles or amorphous carbons [22,34]. Hence additional steps are required to purify them before using them for nanocomposite development [22,35-45]. Furthermore, stringent controls of the processing conditions are required during initial purification and functionalization, as well as during the sintering step, in order to prevent damage to the CNT structure.

2.1.2. Processes used for Sintering Ceramic-based Nanocomposites

Techniques based on powder metallurgical principles have been the primary route for development of bulk ceramic nanocomposites, whether particulate or fibre reinforced. In a broader sense, the major issue concerning the sintering of particulate ceramic nanocomposites lies in the attainment of near theoretical density, while at the same time minimizing the microstructural coarsening of particulate reinforced nanocomposites [1,2] and preventing damage to the carbon nanotubes in CNT-reinforced nanocomposites [22,46]. However, it has been observed that incorporation of refractory and covalently bonded nanosized particles (such as SiC) in the starting powder mixture severely inhibit densification and virtually render the attainment of dense nanocomposites via conventional pressureless sintering impossible [1,2,4-6,47-

54]. On a similar note, the presence of carbon nanotubes in the starting powder mixtures of CNT reinforced nanocomposites leads to poor densification kinetics [22-24,55,56]. Also, especially for nanosized oxide particles, excessive particle/grain coarsening during the later stages of sintering often renders the retention of nanocrystalline grains/particles in the sintered product being extremely difficult using conventional sintering techniques [1,2,6,12]. In order to address such issues, use of pressure assisted sintering techniques [1,2,4-6,48-66], such as hot pressing, or advanced sintering techniques involving simultaneous applications of external pressure and electric field [1,6,67-78], such as spark plasma sintering (SPS), have been explored.

One of the most widely investigated particulate reinforced ceramic nanocomposite systems, viz. Al_2O_3 -SiC, has been routinely processed via hot pressing (Fig. 2.3a) in various research laboratories ever since it was first developed by Niihara using the same technique [1,2,4-6,48-54]. On a similar note, pressure assisted sintering techniques have been successfully employed to regularly develop polycrystalline ceramics and glass based nanocomposites containing both single walled as well as multiwalled carbon nanotubes (Fig. 2.3b) [19,22,46,55,56,60-66]. The advent of SPS not only makes it feasible to develop dense bulk nanocomposites based on even the most refractory ceramics [1,2,6,67-71] in a much shorter time, it has also helps in preserving the structural integrity of CNTs even when high sintering temperatures are required for developing refractory ceramic - CNT nanocomposites [72-78]. Figs. 2.3c and d present typical TEM micrographs of nano/nano composite, as obtained with Electric Field Assisted sintered (EFAS) Si_3N_4 -SiC [71], and inter/intra-granular nanocomposite, as obtained with SPS processed WC - 6 wt.% ZrO_2 [70], respectively.

Fig. 2.3e shows the presence of nanotubes on a fractured surface of SPS processed Si_3N_4 - 2 vol.% SWCNT nanocomposite [78].

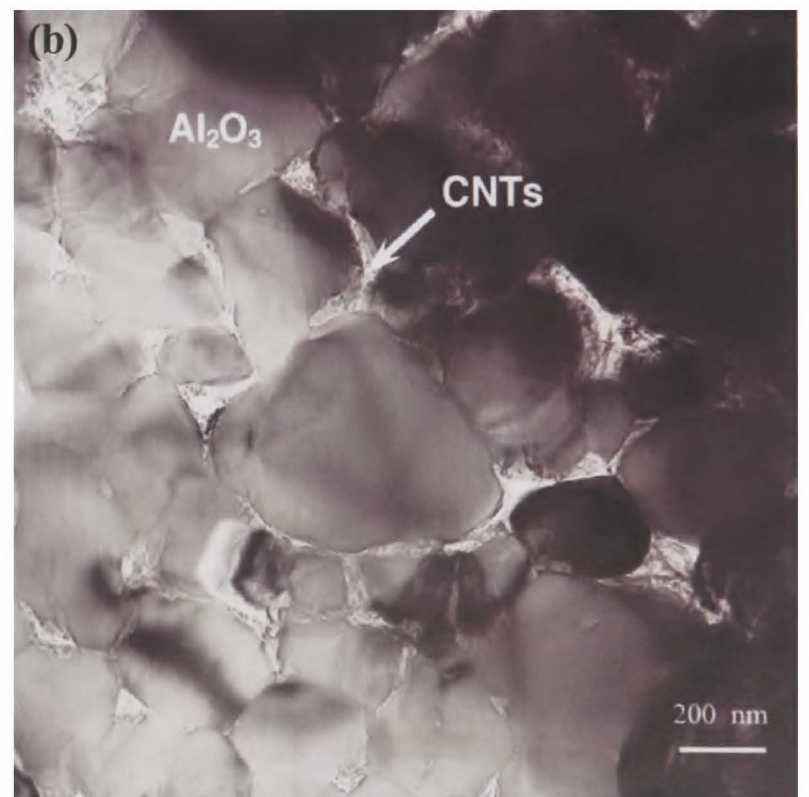
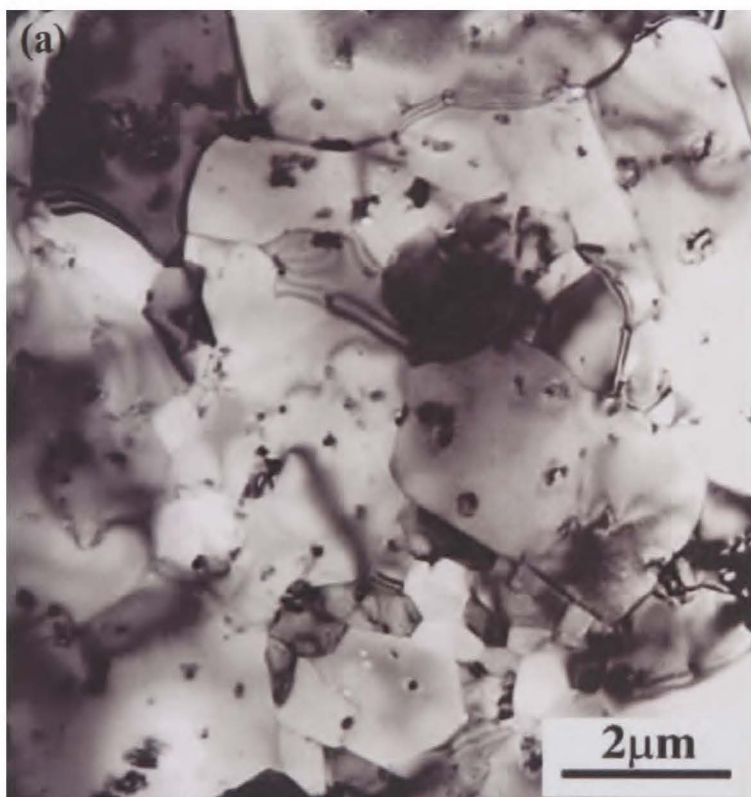
However, due to the expenditure involved and the ability to fabricate only simple shapes of small dimensions, such pressure and electric field assisted sintering techniques have not yet been adopted as commercial processes for mass production of bulk ceramic nanocomposites. Considering that pressureless sintering is one of the most conventional and cheap methods widely used to sinter ceramics, research efforts have been directed towards development of processing schemes which would allow successful fabrication of ceramic nanocomposites.

2.1.2.1. Development of ceramic nanocomposites via Pressureless Sintering

In order to successfully develop dense ceramic nanocomposites via pressureless sintering, researchers have tried to devise various modifications of the sintering cycles or the conditions involved during sintering [7,53,79-83]. Furthermore, the use of dopants or sintering aids to accrue the densification kinetics, while at the same time hinder microstructural coarsening, have also been found to aid in the development of dense nanostructured ceramics via pressureless sintering [7,53,79-83]. However, it must be noted here that even though certain modifications based on pressureless sintering have allowed the development of dense particulate reinforced ceramic nanocomposites [7,53,79-83], reports concerning the development of CNT reinforced ceramic nanocomposites via pressureless sintering [84] are extremely scarce.

With respect to particulate reinforced ceramic nanocomposites, presence of refractory SiC nanoparticles severely inhibits the densification of Al_2O_3 -SiC nanocomposites using pressureless sintering technique [1,2,4-6,47,48,53,79-83]. In this regard, it has been observed that use of Y_2O_3 [53,79-82] or CeO_2 [83] as sintering aids allow near

theoretical densification of Al_2O_3 -SiC nanocomposites via pressureless sintering at modestly lower temperature of $\sim 1600^\circ\text{C}$. It has been proposed that reaction of Y_2O_3 with SiC lead to the formation of a thin SiO_2 - Y_2O_3 - Al_2O_3 glassy phase or segregated layer along the grain boundaries, which increases grain/phase boundary diffusivity, thereby improving sintering rate [53]. However, such benefits from the use of sintering aids are limited only for a very narrow composition-processing window and for nanocomposites containing not more than 2 vol.% SiC. Furthermore, doping with suitable amount of MgO and pressureless sintering in nitrogen atmosphere has also been reported to allow near theoretical densification of Al_2O_3 - 5 vol.% SiC nanocomposite powders, albeit at a higher temperature of $\sim 1750^\circ\text{C}$. The dense ‘nanocomposites’ were observed to contain nanosized intragranular SiC particles (50 - 200 nm), but relatively coarse inter granular SiC particles (up to $\sim 0.5\ \mu\text{m}$) (Fig. 2.3f) [82].



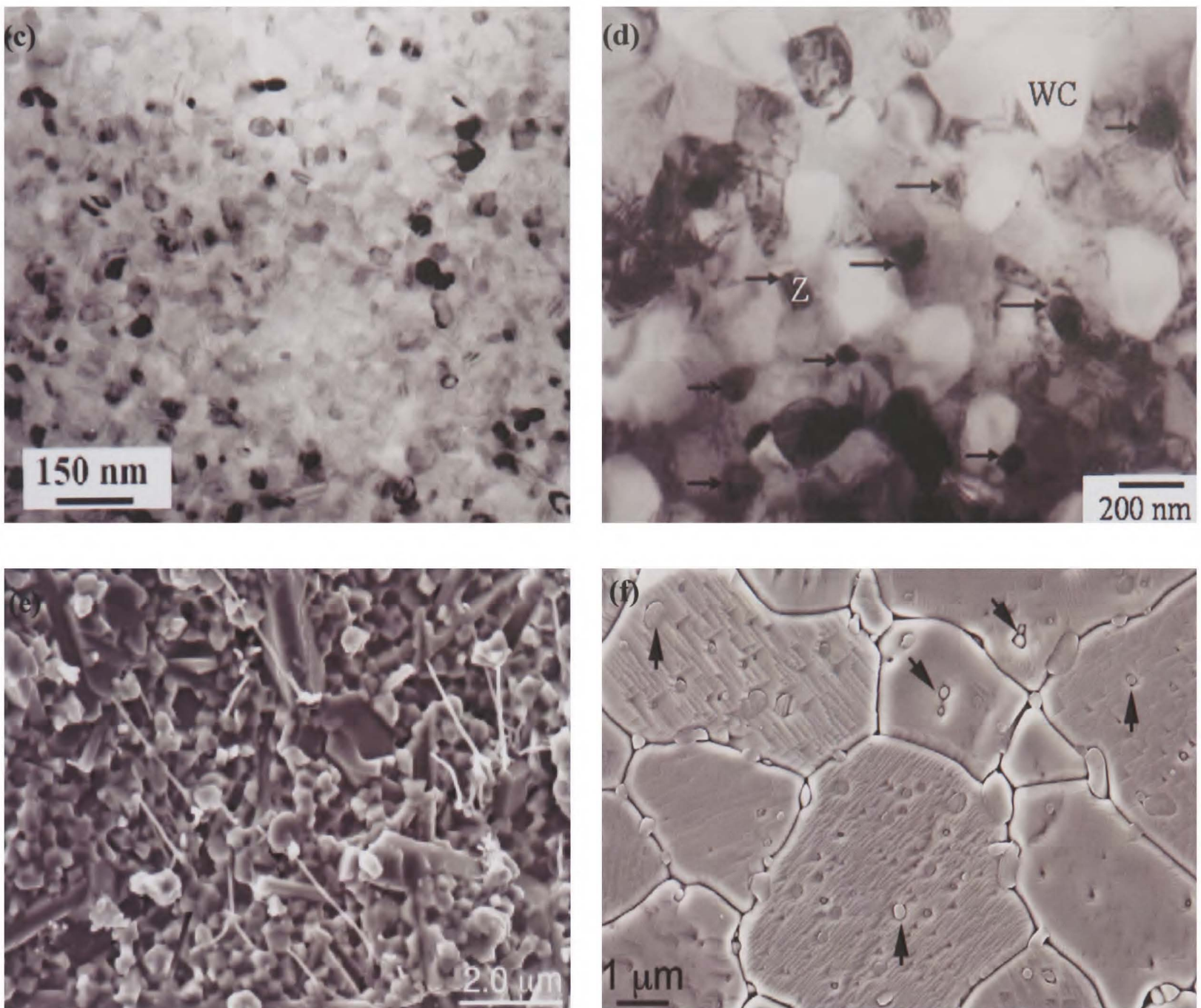


Fig. 2.3. TEM micrographs corresponding to typical microstructures of (a) inter/intra-granular Al_2O_3 -SiC nanocomposite fabricated by hot pressing at 1700°C [50]; (b) Al_2O_3 - 3 vol.% MWCNT nanocomposite developed by hot pressing at 1600°C . Note that the nanotubes are present only along the matrix grain boundaries [60]; (c) Si_3N_4 -SiC nano/nano-composite fabricated using SPS at 1450°C of powders derived via polymer pyrolysis [71]; (d) WC - 6 wt.% ZrO_2 nanocomposite fabricated using SPS at 1300°C for 5 min (arrows indicate the ZrO_2 nano particles) [70]. SEM images of (e) fractured surface of Si_3N_4 - 2 vol.% SWCNT nanocomposite developed using SPS at 1600°C without holding [78]; (f) polished and thermally etched surface of Al_2O_3 - 5 vol.% SiC (0.05 wt.% MgO) nanocomposite sintered at 1780°C using pressureless sintering [82].

2.1.2.2. Development of Particulate Ceramic Nanocomposites via Aging

One of the possible routes to develop particulate reinforced ceramic nanocomposites is in-situ formation of nano-sized dispersoids via aging of supersaturated solid solutions. By careful control of the temperature and time of aging, growth of the nucleated second phase precipitate particles can be controlled to obtain a desirable size, morphology and dispersion of the second phase particles. However, to date there are very few literature reports which explore the possibility of development of Al_2O_3 -based ceramic nanocomposites via such precipitation techniques. This may be at least partly due to the fact that most ions present negligible solubility in Al_2O_3 due to their comparatively larger radii, different charge under normal atmospheric conditions with respect to Al^{3+} and different crystal structure of their oxides compared to that of α - Al_2O_3 [85-89]. Hence in the few investigations exploring this technique, only limited amounts of the precipitated secondary phase particles could be formed [85,89].

One of the earliest indications of precipitation from supersaturated solid solution in Al_2O_3 ceramics is the formation of needle shaped precipitates (possibly TiO_2) observed in star sapphire [90,91]. However, the needles formed in such star sapphires are usually several hundreds of micrometers in length (Fig. 2.4a). Despite the coarseness of such precipitates, reports do exist which suggest that star sapphire possess improved hardness and fracture strength with respect to pure sapphire [90].

The use of similar precipitation rates for the formation of secondary phases in Ti containing Al_2O_3 has also been explored for polycrystals. Sub-micron sized TiO_2 needles within matrix grains of polycrystalline Al_2O_3 , along with coarser Al_2TiO_5 precipitates at the triple point corners of the matrix grains, were obtained during heating in an oxidizing atmosphere of $(\text{Al}_{1-x}\text{Ti}_x^{3+})_2\text{O}_3$ solid solutions containing a maximum of only 0.6 cation% Ti [89].

In a more recent investigation, Wang et al. [85] developed Al_2O_3 -based nanocomposites, by precipitation of nanocrystalline magnesium aluminium spinel during aging in a reducing atmosphere (H_2) of a supersaturated solid solution of Al_2O_3 containing Mg^{2+} and Ti^{4+} ions (Fig. 2.4b). However, due to limited solubility in Al_2O_3 , only a maximum of 2 mol% ($\text{MgO} + \text{TiO}_2$) can be incorporated during solution treatment which limits the volume fraction of the second phase particles that can be precipitated out during the aging treatment.

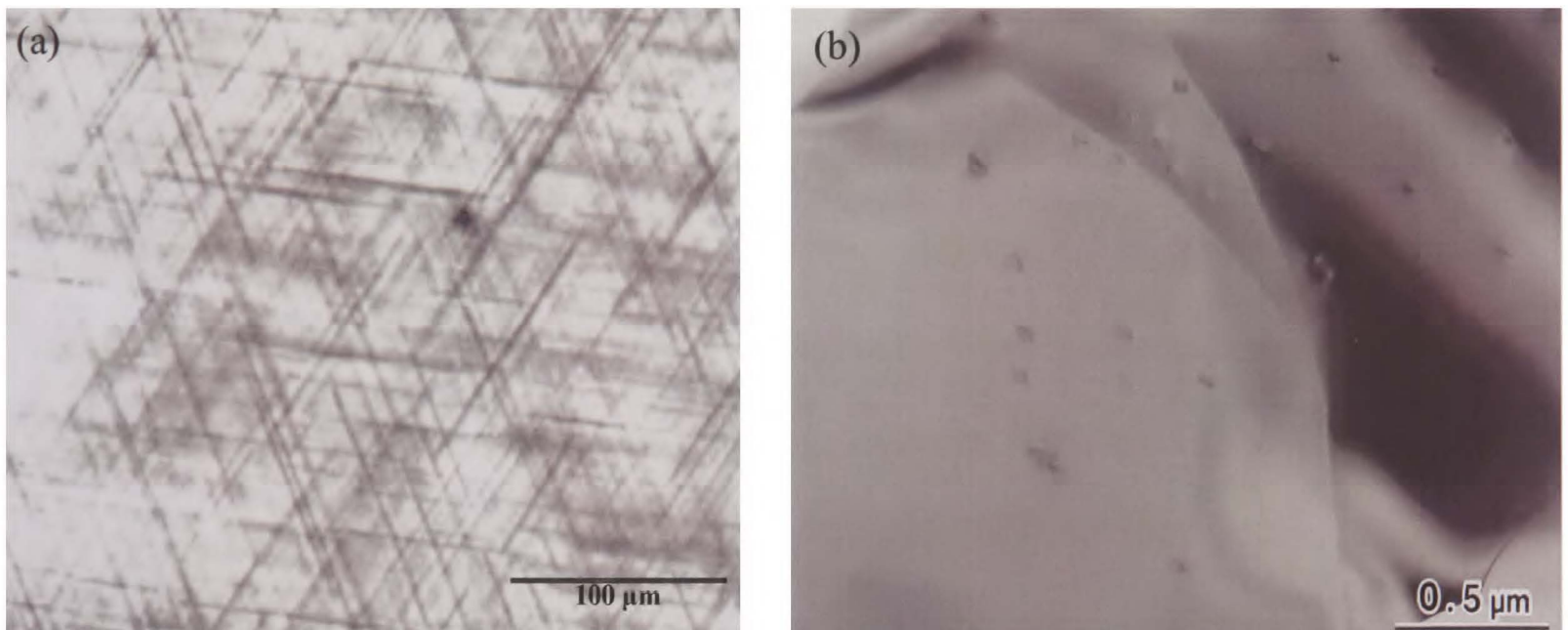


Fig. 2.4. (a) Photomicrograph showing needle/lath shaped precipitates in ‘star sapphire’, formed during aging of 0.5 cation% Ti doped sapphire [90]; (b) TEM micrograph of the Al_2O_3 - MgAl_2O_4 nanocomposite prepared via aging of $(\text{Al},\text{Ti}^{4+},\text{Mg})_2\text{O}_3$ solid solution under reducing atmosphere at 1300°C for 5 h [85].

2.2. Mechanical Properties of Particle Reinforced Al₂O₃-based Nanocomposites

Among different oxide ceramics, alumina and alumina-based composites are probably the most widely used materials for various structural and wear resistance applications. Hence it is quite understandable that a majority of the research investigations on the development and investigation of mechanical and tribological properties of bulk ceramic based nanomaterials have been focused on Al₂O₃-based nanocomposites [1,2,4-6,47-54,58,79-82].

With regard to monolithic Al₂O₃, it has been observed that reduction of grain sizes to the nanosized regime results in considerable improvement in the hardness [1,92,93]. However, nanocrystalline monolithic alumina does not possess improved fracture toughness with respect to conventional brittle monolithic Al₂O₃. Consideration of the fact that modest fracture toughness and fracture strength of ceramics are one of the major factors limiting their structural applicability, research investigations have mostly been directed towards development of Al₂O₃-based nanocomposites where it is believed that nanosized particulates dispersed in Al₂O₃ might lead to toughening and strengthening of the matrix [1,2,4-6,47,48,51-53,58,79-82,93-101]. A comparison of the mechanical properties of the various alumina based nanoceramics/nanocomposites with conventional alumina is presented in Fig. 2.5. However, care must be taken while comparing the different results since factors such as matrix grain size and techniques used for measuring the properties also affect the experimental results.

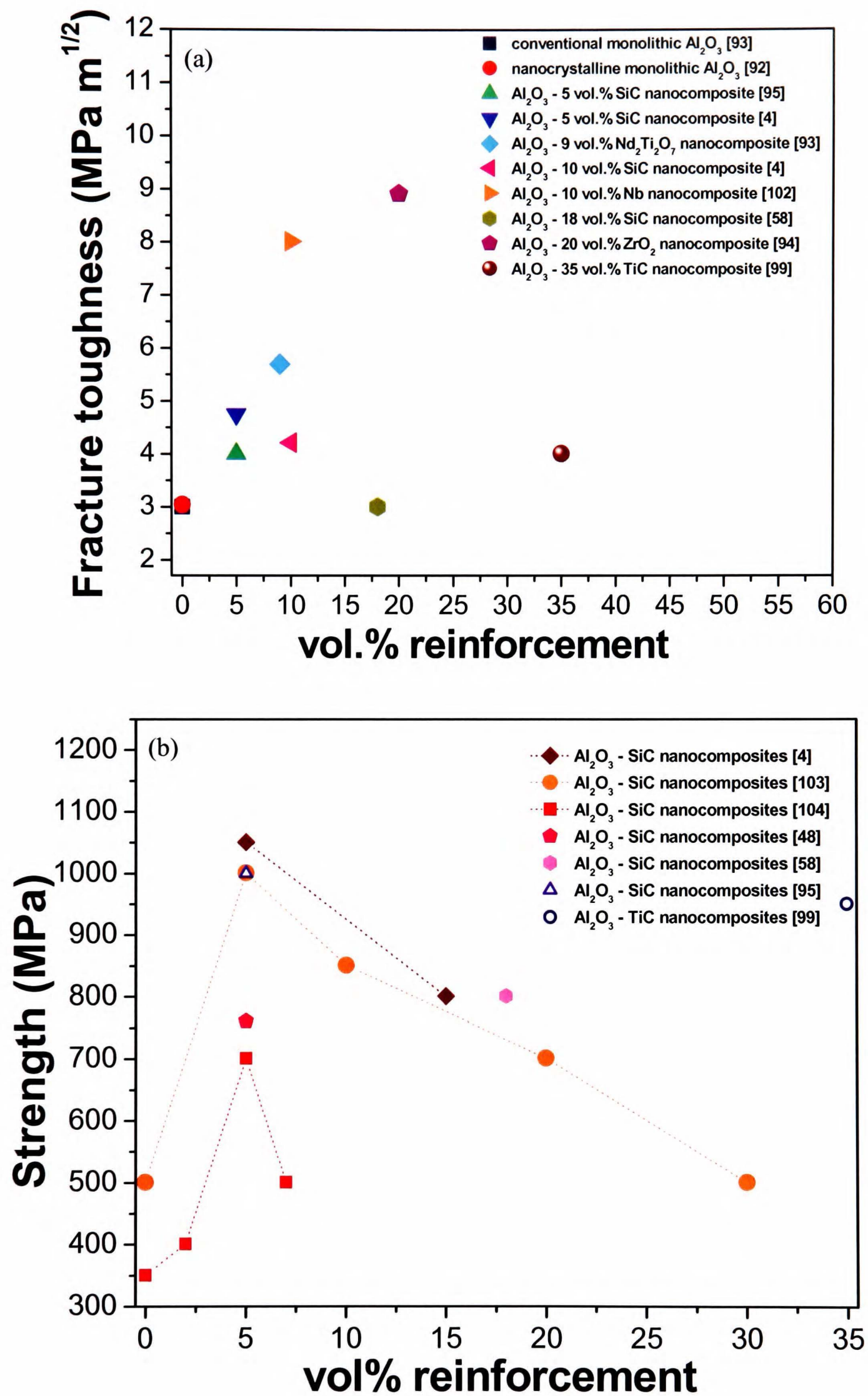


Fig. 2.5. Comparison of (a) fracture toughness and (b) flexural strength of various particulate reinforced nanocomposites based on Al₂O₃. The results obtained during the same work are joined by dotted lines in (b).

2.2.1. Al₂O₃ - SiC Particulate Nanocomposites

Ever since the pioneering work of Niihara [4], which reported that nano-SiC particulate reinforcements, in amounts as low as 5 vol.%, can lead to significant increase in fracture strength (~ 1 GPa, compared to ~ 350 MPa for monolithic Al₂O₃), along with an improvement in fracture toughness (~ 5 MPa m^{1/2}, compared to ~ 3 MPa m^{1/2} for monolithic alumina), several investigations have been made regarding the mechanical behaviour of Al₂O₃ - SiC nanocomposites [1,2,4-6,47-54,79-83,101,103,104]. In the same work, Niihara also reported that the Weibull modulus of the Al₂O₃ - 5 vol.% SiC nanocomposites (~ 13.6) was significantly higher than that of monolithic Al₂O₃ (~ 6.5), signifying the improved reliability of the nanocomposites [4]. This was attributed to the annihilation of abnormal grain growth caused by the pinning effect of the nano SiC particles. Another remarkable result concerning the mechanical properties of Al₂O₃-SiC nanocomposite, has been the achievement of extremely high indentation toughness of ~ 10 MPa m^{1/2} for hot pressed (1650°C) Al₂O₃ - 5 vol.% SiC [105]. In fact most of the investigations, concerned with the evaluation of mechanical properties of hot pressed Al₂O₃-SiC nanocomposites report enhanced fracture toughness and strength for the nanocomposites in comparison to monolithic alumina as well as composites containing coarser matrix/reinforcement grain sizes [1,2,4-6,47-54,79-83,103-108]. However, the extremely high strength reported by Niihara et al. [4] and the fracture toughness reported by Wang et al. [105], have never been reproduced for hot pressed Al₂O₃ - 5 vol.% SiC nanocomposites. For example, Zhao et al. [48] reported a flexural strength of only ~ 760 MPa for hot pressed Al₂O₃ - 5 vol.% SiC nanocomposites, as compared to the flexural strength of ~ 500 MPa for monolithic Al₂O₃. On a different note, it was observed in the same work that after annealing the strength of the Al₂O₃ - 5 vol.% SiC nanocomposites

improved from ~ 760 MPa to ~ 1 GPa. Such observations are in agreement with the earlier report of Niihara [4], although Niihara had obtained much higher strengths of ~ 1.5 GPa for the annealed Al_2O_3 - 5 vol.% SiC nanocomposites. Davidge et al. [106] observed that even though Al_2O_3 - SiC nanocomposites possess improved strength with respect to monolithic Al_2O_3 , no apparent improvement in toughness could be recorded with the nanocomposites. In a work exploring the effects of different precursors and routes for generating the starting powder mixtures on the mechanical properties of hot pressed Al_2O_3 - 10 wt.% SiC nanocomposites, Borsa and co workers [107] observed that the nanocomposites possessed virtually the same strength as monolithic Al_2O_3 , irrespective of the processing route.

2.2.2. Mechanisms Responsible for the Improvements in Mechanical Properties

Various reasons have been cited to account for the observed improvements in the mechanical properties for the nanocomposites with respect to the monolithic ceramics [1,5,103,104,109-119]. However, to date there has been no unified consensus with respect to the primary strengthening/toughening mechanisms. This also stems partly from the disagreement between the various experimental results reported by different research groups [1,2]. Hence it is believed that such improvements are a result of contribution from different micro mechanisms operating simultaneously in different nanocomposites.

The thermal expansion co-efficient mismatch between the matrix and the nanosized second phase particles have been deemed responsible by many researchers for the toughening and strengthening achieved in the nanocomposites [1,5,103-105,113-115,117,119]. This mismatch leads to the development of localized residual stresses

within/around the reinforcements. In particular, tensile residual stresses of ~ 200 GPa in the Al_2O_3 matrix and compressive residual stress of ~ 1.8 GPa in the SiC nanoparticles has been experimentally measured using fluorescence microscopy for hot pressed Al_2O_3 - SiC nanocomposites [120,121]. Furthermore, using mathematical models for residual stress development Awaji et al. [114] had estimated that a tensile residual stress of ~ 1.2 GPa can exist in the Al_2O_3 matrix grains, along with maximum shear stress of ~ 1.7 GPa at the Al_2O_3 - SiC interfaces. It is believed that tangential tensile stress in the Al_2O_3 grains result in “strengthening” of the grain boundaries and “weakening” of the grains. Such weakening of matrix grains, along with the development of compressive residual stresses within the second phase particles have been reported to cause crack deflection by the particles present along the matrix grain boundaries, resulting in the change in fracture mode from intergranular to transgranular [1,5,103-105,113-115,117,118,119]. It must be mentioned here that despite the debate over improvement in mechanical properties and the mechanisms responsible for them, the transgranular fracture mode for the Al_2O_3 - SiC nanocomposites, as opposed to the intergranular fracture for monolithic Al_2O_3 , has been confirmed by nearly all researchers working on such nanocomposites [1,5,48-52,103,104,113-115,117-119,122] (Fig. 2.6). It has also been estimated that a change in fracture mode to transgranular can itself lead to considerable improvement in fracture toughness of alumina [123]. In two different works Sun et al. [104] and Levin et al. [124] have successfully correlated the experimentally measured fracture toughness for Al_2O_3 - SiC nanocomposites with those theoretically estimated using models based on change in fracture mode due to thermal expansion mismatch induced residual stresses. Both of them predict that the nanocomposites should possess maximum strength and fracture toughness at some optimum SiC content (~ 5 vol.%).

In this regard, it can be observed from Fig. 2.5 that even though most of the investigated nanocomposites possess higher toughness and strength compared to that of conventional alumina ceramics, the zenith is reached at ~ 5 vol.% SiC reinforcement. Such a variation of strength/fracture toughness, with reinforcement content, can be explained by the fact that below the threshold amount (5 vol.%), the grain boundaries are not fully strengthened by the compressive residual stress, but further increase (above 5 vol.%) in nano-reinforcement content weaken the matrix grains (by residual traction) considerably. Additionally, the reduction of strength with increased additive content can also be partly attributed to agglomeration effect [5,116].

Another toughening mechanism has been proposed, which is also based on the residual stress development, especially near the reinforcement/matrix interfaces. Such stresses can create defects in the form of sessile dislocations near the interfaces, which can act as nucleation sites for micro/nano-crack formation at the crack tip of a propagating crack [113,114]. If such cracks are lower than some critical size and are properly oriented with respect to applied stress and larger pre-existing cracks, micro/nano-cracking can expand the size of the fractal process zone (FPZ), resulting in fracture toughness increment [113,114]. Furthermore, such micro cracking within the matrix grains is also believed to contribute towards the change in fracture mode to transgranular fracture for the nanocomposites. The presence of extensive dislocation activity, including sub grain boundaries, near the secondary phase particles has been specifically observed by many researchers, including Niihara [4] and Anya [109]. The shear stresses present at the Al_2O_3 - SiC interfaces (~ 1.7 GPa), as theoretically estimated by Awaji et al. [114], are believed to be sufficient to generate dislocations around the particles. Additionally, the presence of numerous cleavage steps, which

increase in density with SiC content [4,48,114,125], in the transgranular fracture surfaces observed for the Al_2O_3 - SiC nanocomposites have also been suggested to present indirect evidence for the existence of micro cracking around the second phase particles [114].

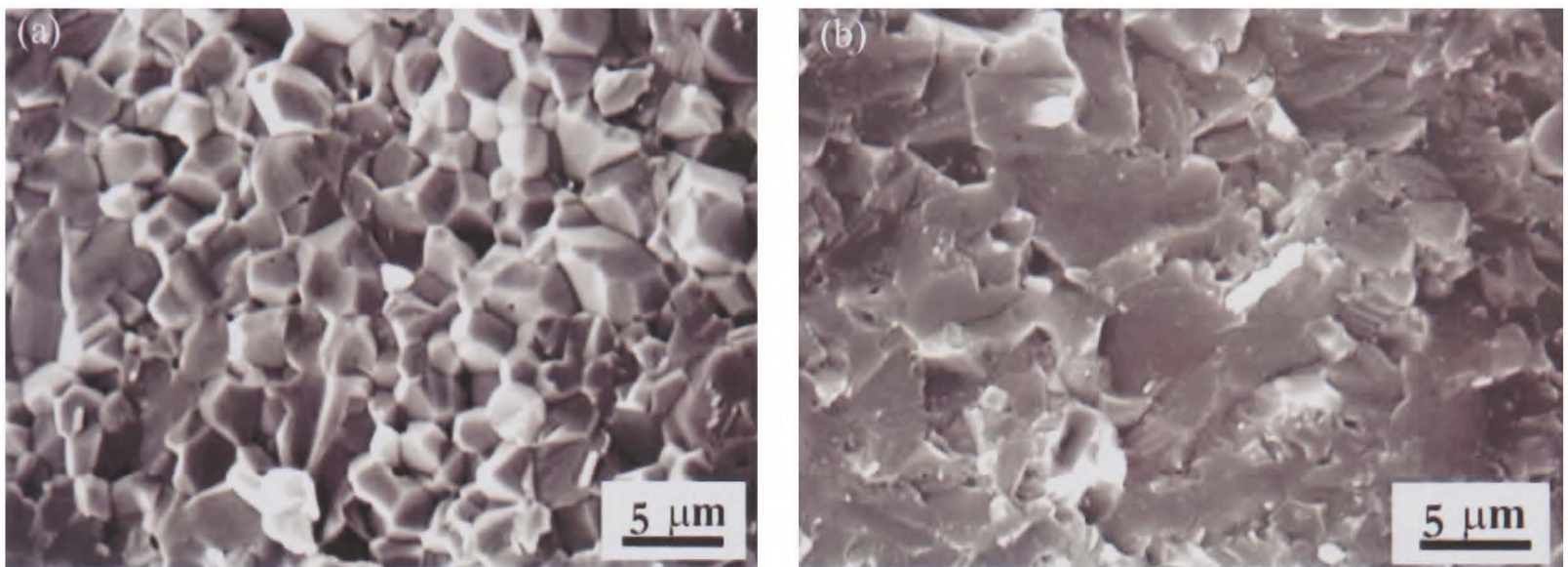


Fig. 2.6. Scanning electron microscopy (SEM) images of fractured surfaces of (a) monolithic Al_2O_3 showing typical intergranular fracture mode; (b) Al_2O_3 - 1 vol.% SiC nanocomposite showing transgranular fracture [54]. Note that only 1 vol.% SiC is sufficient to change the fracture mode from intergranular to transgranular.

In addition to the aforementioned mechanisms responsible for the improvement in mechanical properties, in particular the strength of nanocomposites, reduction in flaw size and density in the nanocomposites due to microstructural refinement is also cited as another major reason for the enhanced strength [116,118,125]. It is believed that soft alumina agglomerates, which often serve as fracture origins and strength limiting flaws in monolithic alumina, are destroyed during the grinding/milling step in the presence of hard nanosized second phase particles like SiC [5]. Furthermore, it has also been demonstrated that the nanocomposites develop surface compressive residual

stress higher in magnitude with respect to monolithic Al_2O_3 [48,126]. This is in turn believed to be partly responsible for the improvement in the mechanical properties.

2.2.3. Other Al_2O_3 -based Particulate Nanocomposites

Zhan et al. [94] developed ZrO_2 toughened Al_2O_3 nanocomposite via combination of HEBM and SPS of γ -alumina powders, mixed with 3 mol% yttria stabilized zirconia (3Y-TZP). The Al_2O_3 - 20 vol.% ZrO_2 nanocomposite possessed hardness of ~ 15.2 GPa and fracture toughness of $\sim 8.9 \text{ MPa m}^{1/2}$. The fracture toughness increment was reportedly due to ferroelastic domain switching of the ultra-fine t- ZrO_2 . Despite the presence of significant amount of softer ZrO_2 phase (for fracture toughness increment), considerably high hardness was retained, which was believed to be a direct consequence of the microstructural refinement down to nanocrystalline regime.

In another work, combination of HEBM and SPS (1480°C , 4 min) of powder mixture of Ti, graphite and Al_2O_3 led to the development of Al_2O_3 - 35 vol.% TiC nanocomposite [99]. The nanocomposites exhibited superior fracture strength of ~ 950 MPa, with respect to hot pressed Al_2O_3 -TiC composites having coarser grains.

As opposed to most Al_2O_3 -based nanocomposites, an attempt to develop Al_2O_3 - 5 wt.% TiN nanocomposites via hot pressing revealed that TiN nanoparticles do not improve the strength of Al_2O_3 [51]. Furthermore, no change in fracture mode to transgranular fracture was observed for the Al_2O_3 - TiN nanocomposites, as opposed to the Al_2O_3 - SiC nanocomposites. In fact, it was found that TiN particles actually weaken the matrix grain boundaries instead of strengthening them. The detrimental factor is believed to be the formation of TiO_2 at the $\text{Al}_2\text{O}_3/\text{TiN}$ interfaces [127].

A novel approach towards fracture toughness increment of brittle alumina involves the incorporation of nano-scaled piezoelectric ceramic phase in the alumina matrix. In this regard, Zhan et al. [93] developed Al_2O_3 - $\text{Nd}_2\text{Ti}_2\text{O}_7$ nanocomposite via SPS. The Al_2O_3 - 9 vol.% $\text{Nd}_2\text{Ti}_2\text{O}_7$ nanocomposites exhibited a superior fracture toughness of $5.7 \pm 0.4 \text{ MPa m}^{1/2}$. The fracture toughness increment was believed to be due to the conversion of mechanical energy to electrical energy during localized deformation in the presence of piezoelectric second phase ($\text{Nd}_2\text{Ti}_2\text{O}_7$). In their follow-up work, γ - Al_2O_3 - 7.5 vol.% BaTiO_3 nanocomposite was densified using SPS [100] and a similarly high fracture toughness of $\sim 5.3 \pm 0.3 \text{ MPa m}^{1/2}$, presumably due to the domain switching effect, was observed [93,100,128,129].

It must be noted that even though significantly improved properties have been achieved with the different Al_2O_3 -based nanocomposites, the nanocomposites have been developed using either hot pressing or SPS, which does not render them suitable for large scale commercial productions.

2.3. Tribological Properties of Particulate Reinforced Ceramic Nanocomposites

Ceramic-based materials are potential candidates for use in various tribological applications. Hence, research activities have been devoted towards exploring the possibilities for further improvement of wear resistance of various structural ceramics so as to render them suitable for extensive use in demanding tribological applications. In this regard, experimental observations point towards the possibility of further improvement of the tribological properties by developing ceramic based nanocomposites [1,2,6,49,50,51,130-138]. In fact, amongst the various properties of

structural ceramics, the most remarkable and reproducible improvement produced by reinforcement of the matrix by nanosized particles, has been in the tribological properties [1,2,6,49,50,51,130-135]. Various possible reasons, with respect to the type of material, operating conditions and dominant wear mechanisms, have been cited for the superior wear resistance possessed by ceramic nanocomposites.

2.3.1. Understanding the Tribological Behaviour of Ceramic Nanocomposites

The characteristic difference between conventional structural ceramics/composites and ceramic nanocomposites is the significantly refined microstructural scale for the latter. The presence of nanocrystalline grains or nanosized dispersoids has been reported to result in increased hardness [1,2,4,5,139,140]. Among various other reasons, this higher hardness is believed to be partly responsible for the improved wear resistance of different ceramic nanocomposites. On a similar note, from an empirical equation developed by Archard [141];

$$v = KWx/H \quad (2.1)$$

where v is the wear volume, W is the normal load, x is the sliding distance, H is the hardness and K is the probability of formation of a wear particle during a particular asperity interaction, it can be observed that the amount of material lost due to wear (v) is inversely related to the hardness (H) of the worn material.

One of the most dominant wear mechanisms observed for most structural ceramics, especially during severe wear, is brittle fracture induced grain pull-out. For material removal by this mechanism, the wear rate is dependent on the dimensions of the individual pull-outs, as well as the rate of pull-out. With respect to the pull-out dimensions, Evans [137] developed a model which predicts that the lateral dimension

of pull-out is proportional to $E^{3/5}/(K_c^{1/2}H^{29/40})$, while the pull-out depth is proportional to $E^{2/5}/H^{3/2}$. Hence, it can be again conceived that higher hardness of ceramic nanocomposites is beneficial in that it results in reduced wear loss by grain pull-out. Furthermore, it has been frequently observed that incorporation of nanoscaled ceramic reinforcements in conventional/nanostructured ceramic matrix (ceramic nanocomposites) results in a modest increase of fracture toughness (see section 2.2) [1,2,4,5,139,103,104,109-119], which should lead to further improvement of the wear resistance of ceramic nanocomposites. Hence, such improvements in bulk mechanical properties are believed to cast their influence on the tribological properties, resulting in improved wear resistance for bulk ceramic nanomaterials.

Careful comparison of various literature reports concerning the tribological behaviour of the widely investigated Al_2O_3 -SiC nanocomposites reveals that although the nanocomposites containing 5 vol.% SiC exhibit an excellent combination of bulk mechanical properties [1,2,4,5,103,104,48,58,95,124] (Fig. 2.2), the presence of higher SiC contents (10 - 20 vol.%) often results in better tribological properties [2,49,50,130-134]. Hence, the requirement of a higher volume fraction of nanosized reinforcements for improving wear resistance implies that the reasons for better tribological performance of nanoceramic composites are not solely restricted to the improved bulk mechanical properties.

It has been observed that the presence of suitable nanosized reinforcements often changes the fracture mode from intergranular (for monoliths) to transgranular (nanocomposites). Various plausible reasons behind the change in fracture mode are discussed earlier (see section 2.2.2). For wear dominated by grain pull-out, such a change in fracture mode is deemed beneficial for the wear resistance because the individual size of the pull-outs as well as the rate of grain pull-out gets considerably

reduced [1,2,49,50]. In this context, investigating the abrasive wear behaviour of Al_2O_3 -SiC nanocomposites, Ortiz-Merino and Todd [50] developed a model based on a simple geometry of crack propagation, which implies that, in a certain grain size range, the mean pull-out dimension is considerably reduced when the fracture mode is predominantly transgranular. A schematic representation, comparing the probable pull-out dimensions in the presence of intergranular and transgranular fracture mode is shown in Fig. 2.7a. It is also believed that pull-out in Al_2O_3 is caused by cracking nucleated by plastic deformation [49,50]. The presence of intragranular SiC particles in the nanocomposites block the development of twins and dislocation pileups, thus limiting their length and associated stress concentration to below those required for crack nucleation.

In support of the above hypothesis, it must be noted here that the worn surfaces of monolithic Al_2O_3 and Al_2O_3 -SiC nanocomposites always possess contrasting appearances. While the worn surface of monolithic alumina is generally rough due to the presence of numerous pull-outs as a result of intergranular fracture, the worn surfaces of Al_2O_3 -SiC nanocomposites (> 5 vol.% SiC) are comparatively smooth with negligible presence of pull-outs, which are mostly formed due to transgranular fracture [1,2,49,40,130-134]. SEM micrographs of some typical worn surfaces corresponding to monolithic Al_2O_3 and Al_2O_3 -SiC nanocomposite are presented in Fig. 2.7b,c.

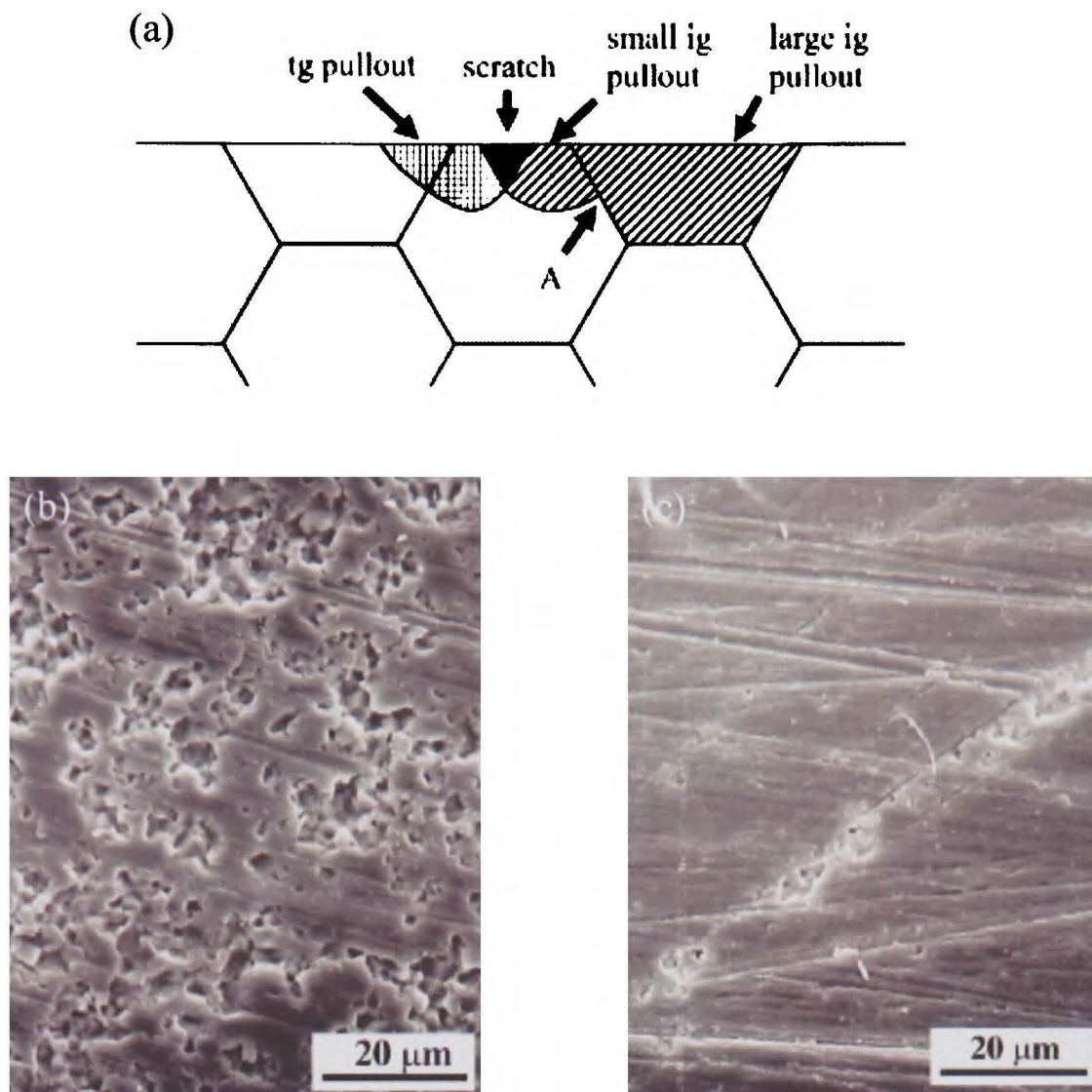


Fig. 2.7. (a) Schematic representation of the Influence of fracture mode on the probable pull-out dimensions. SEM images of worn surfaces of (b) monolithic Al_2O_3 showing rough surface caused by numerous pull-outs and (c) Al_2O_3 - 10 vol.% SiC nanocomposite, depicting significantly reduced contribution of pull-out induced wear for the nanocomposite, implying higher wear resistance for the same [50].

It has been observed that during operation most ceramics undergo a load dependent or time dependent transition from mild wear to severe wear [1,2,130-134,142]. It has been suggested that dislocation plasticity, that is deformation controlled wear, is dominant in the mild wear regime, whereas catastrophic intergranular fracture and pull-out comprises the severe wear regime [2,130-134,143]. In this context, the benefits of ceramic nanocomposites arise from the fact that during wear of such materials the transition from mild to severe wear is either completely eliminated or

significantly delayed. During the deformation controlled initial mild wear regime dislocations and twins tend to pile up against the grain boundaries resulting in stress concentrations and concomitant microcracking along the grain boundary, thus laying the seed for the transition to intergranular fracture controlled severe wear. Owing to considerable improvement in hardness of ceramic nanocomposites, the rate of accumulation of plasticity controlled damage and concomitant tensile stress during the initial deformation-controlled wear is significantly reduced. Furthermore, the finer matrix grain sizes and presence of intragranular nanosized reinforcements in nanocomposites reduces the length of the dislocation pile ups and hence the stress concentration at the grain boundaries, thus lowering the probability of formation of grain boundary micro cracks.

2.3.2. Overview of the Tribological Properties of Al₂O₃-based Nanocomposites

Survey of the existing literature reveals that probably the most comprehensive and copious results concerning the tribological behaviour of ceramic nanomaterials in sliding, abrasive or erosive wear modes, have been obtained with Al₂O₃-SiC nanocomposites. The observations that Al₂O₃-SiC nanocomposites exhibited nearly three times improved wear resistance [49,50,51,130-134] and could also be easily ground and polished to a better surface finish [48,54,144-145], as compared to monolithic Al₂O₃, were the preliminary indications of superior tribological performance of nanocomposites over conventional ceramics.

Rodriguez et al. [130] studied the dry sliding wear behaviour of Al₂O₃ and Al₂O₃-SiC nanocomposites against Mg-PSZ at high normal loads (125-150 N) and reported an improved wear resistance for the nanocomposites as compared to unreinforced

alumina by a factor of approximately 3-5, especially at the higher loads. In the same study, the effects of SiC particle size (40-800 nm) on the wear behaviour were also investigated. It was noted that for the ‘composites’ reinforced with ~ 800 nm SiC particles, the transition from mild to severe wear did occur when tested at the higher loads, resulting in poorer wear resistance similar to that of post transition monolithic Al_2O_3 . On the other hand, such a transition never occurred for the ‘nanocomposites’, resulting in smooth appearance of the ‘worn’ surface and lower wear rate. SEM micrographs showing the worn surfaces after sliding wear of monolithic Al_2O_3 , Al_2O_3 - SiC (800 nm) ‘composite’ and Al_2O_3 - SiC (< 200 nm) ‘nanocomposite’ are presented in Fig. 2.8. Note the rough surfaces, characterized by the occurrence of severe intergranular fracture for both monolithic alumina (Fig. 2.8a) and Al_2O_3 - SiC (Fig. 2.8b) ‘composite’, in contrast to the ‘smooth’ surface for the ‘nanocomposite’ (Fig. 2.8c).

Bajwa et al. [131] and Chen et al. [132] further confirmed the non-occurrence of transition to severe wear during sliding of Al_2O_3 -SiC nanocomposites, as against that of pure Al_2O_3 . It was reported that, while the pre-transition wear rates ($1\text{-}2 \times 10^{-8} \text{ mm}^3/\text{N.m}$) were nearly the same for alumina as well as the nanocomposites, the wear rate of alumina increased to $\sim 1 \times 10^{-6} \text{ mm}^3/\text{N.m}$ after transition to severe wear. On the other hand, the wear rate of the nanocomposites decreased slightly, from the initial value ($1\text{-}2 \times 10^{-8} \text{ mm}^3/\text{N.m}$), with sliding distance. It was further noted that among all the nanocomposites, the one containing the highest SiC content (15 vol.%) possessed superior wear resistance, especially at higher loads. Careful observation of the worn surfaces of the nanocomposites after sliding revealed the occurrence of some pitting on the otherwise smooth surfaces (Fig. 2.8c) [132]. It was confirmed that such pitting occurred early on in the test, with the intensity decreasing with duration. From the

observations it is believed that pitting resulted from preferential pull-out of the SiC nanoparticles owing to tensile residual stresses (which is additive to the tensile residual stress imposed by the contacting asperity) in the matrix close to SiC particles. Such an effect is bound to be particularly severe in regions where SiC particles are clustered. Hence, in accordance with the mechanical properties, wear resistance is likely to be improved with improved distribution of SiC particles.

In a more recent work comparing the wear behavior of alumina and Al₂O₃-SiC (2-10 vol.%) nanocomposites under abrasive wear conditions, it was shown that the wear rate and area fraction of surface pull-out were considerably reduced on increasing the amount of SiC dispersions and reducing the grain size of alumina [50]. In another work it was also shown that intragranular particles in alumina suppress the initiation of the surface fracture responsible for production of pull-outs [49]. For the nanocomposite containing 10 vol.% SiC, the abrasive wear rate was found to be improved by a factor of ~ 3.4 over that of pure alumina. Such improvement is in agreement with the results obtained during sliding wear study of monolithic Al₂O₃ and Al₂O₃-SiC nanocomposites, as reported earlier by Rodriguez et al. [130].

On similar notes, Walker et al. [51], Davidge et al. [133], Anya [134] and Sternitzke et al. [146] observed significant reductions in erosive wear rate, accompanied by smooth transgranular fracture, as a result of the dispersion of secondary nanoparticles of SiC in Al₂O₃ matrix. Anya [134] also noted that for $\sim 95\%$ dense monoliths and nanocomposites, the improvement in wear resistance for the nanocomposites is by $\sim 400\%$, as compared to $\sim 200\%$ improvement observed for materials possessing near theoretical density.

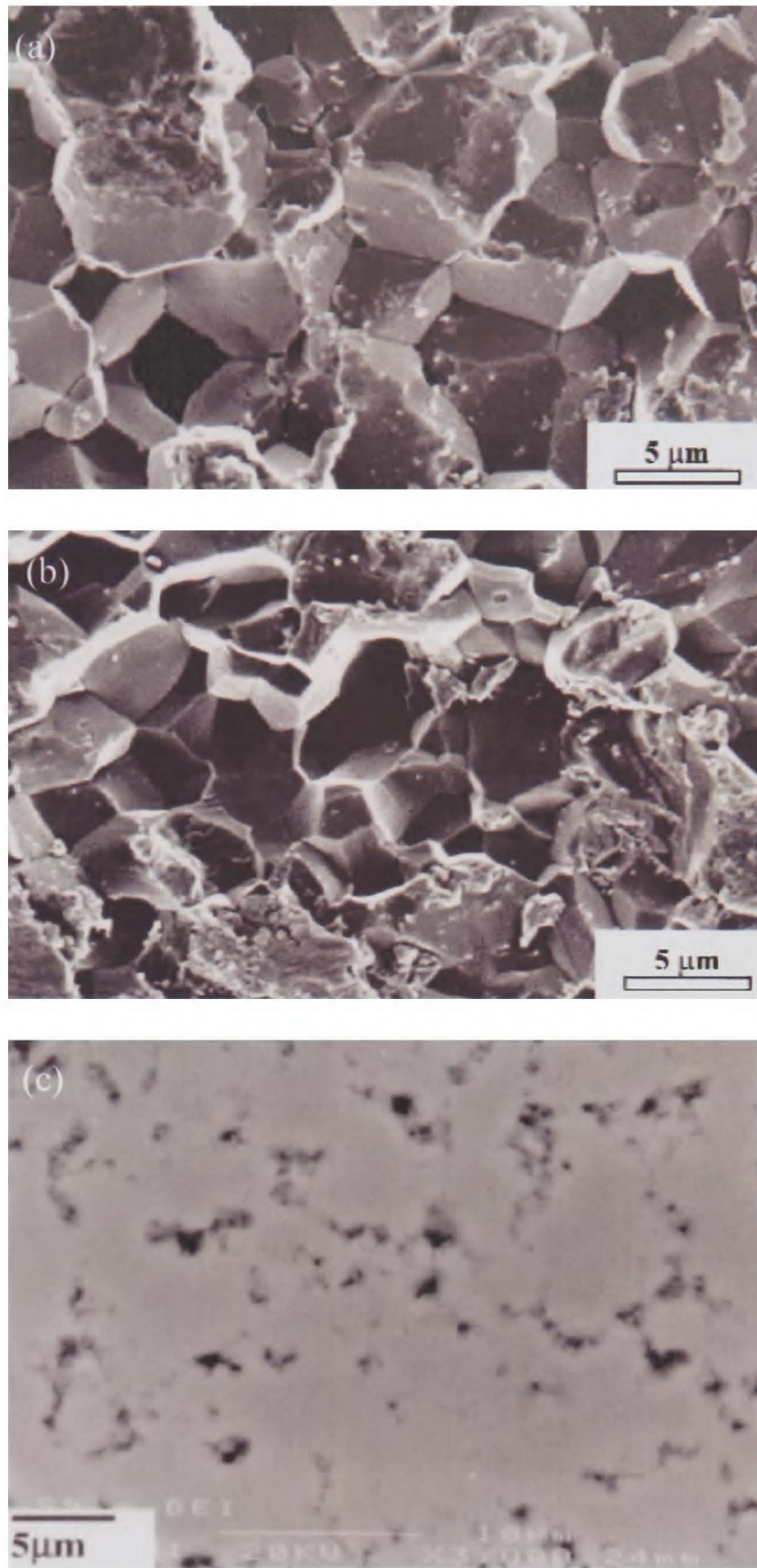


Fig. 2.8. SEM micrographs of worn surfaces of (a) monolithic alumina and (b) Al_2O_3 - SiC (800 nm) 'composite' showing rough surface due to occurrence of predominantly intergranular cracking induced severe wear [130], as against the smooth surface with localized pitting observed for (c) Al_2O_3 - SiC 'nanocomposite' after dry sliding wear test [132].

In an attempt to design wear resistant bio-inert material for femoral head of total hip joint replacement, Lee et al. [135] developed Al_2O_3 - TiO_2 nanocomposites and tested them against Si_3N_4 balls on pin on disc configuration. The sliding wear resistance of the nanocomposite reinforced 10 mol.% TiO_2 was found to be superior to that of monolithic alumina by a factor of ~ 5 . Wang et al. [142] fabricated Al_2O_3 - Al_2TiO_5 ‘nanocomposite’ from TiO_2 -containing Al_2O_3 nanopowder. The effect of grain refinement to the ‘nanosize’ regime on the sliding wear resistance of the as fabricated α - Al_2O_3 / β - Al_2TiO_5 composites is illustrated in Figs. 2.9a,b. It can be clearly observed that significantly lower material damage by pull-out occurs in ultra fine grained (400 nm) α - Al_2O_3 / β - Al_2TiO_5 as compared to the coarser grained (2.2 μm) counterpart [142].

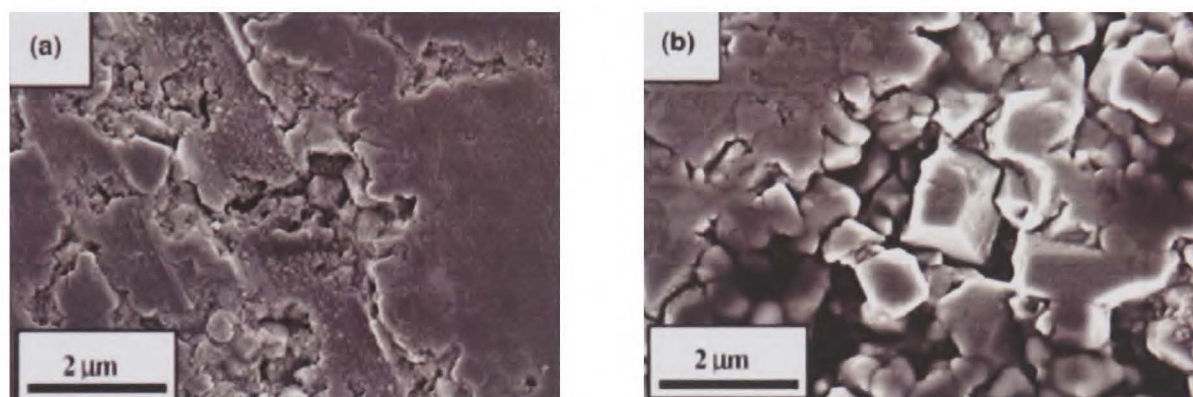


Fig. 2.9. SEM micrographs comparing the worn surfaces of (a) ultra fine grained (UFG) α - Al_2O_3 / β - Al_2TiO_5 composite (1200 min sliding time) with that of (b) coarser grained (CG) α - Al_2O_3 / β - Al_2TiO_5 composite (360 min sliding time) [142].

A summary of the tribological behavior of some of the particulate reinforced Al_2O_3 -based ceramic nanocomposites is presented in Table 2.1. From the above discussion it can be envisaged that in general, matrix grain size refinement, as well as incorporation of nanosized second phase particles, results in improvement in the wear resistance of ceramics. However, the degree of improvement depends on various

aspects. Probably the most important criteria determining the improvement in tribological properties of ceramic nanocomposites is the amount of second phase particles. For some materials, such as Al_2O_3 - SiC nanocomposites, it has been observed that increasing the reinforcement contents results in improved wear resistance [1,2,49,50,130-134]. On the other hand, for other nanocomposites, there exists an optimum reinforcement content which results in best tribological performance [135]. Another important aspect related to improvement in wear resistance is the dependence on the dimension of the nanocrystalline reinforcements. Though some studies clearly elucidate the advantage of using nanosized reinforcements (< 200 nm), as compared to submicron or coarser reinforcements [130,138], any conclusive report of the effect of variation of second phase particle sizes within the nanosize regime is still lacking. In addition to the amount and dimension of the nanosized reinforcements, the distribution of the particles within the matrix is also believed to cast its influence on the tribological behaviour of ceramic nanocomposites. In this context, it is believed that prevention of agglomeration of the second phase particles results in higher wear resistance [132]. However, there is no general consensus yet on the relative effects of the intergranular and intragranular particles and is believed to depend on the concerned material as well as the dominant wear mechanisms.

Material	Counterbody	Tribological conditions	Wear rate	Comparison with conventional material	Comments and wear mechanisms	Reference
Al ₂ O ₃ - 5 vol.% SiC (40 nm) 'nanocomposite'	5 mm diameter MgO-PSZ spheres	Oscillating sliding wear at a speed of 0.15 m/s and 125-150 N load	$\sim 10^{-4}$ mm ³ /m	3-5 times higher wear resistance as compared to conventional monolithic alumina and Al ₂ O ₃ - SiC (800 nm) 'composite' ($\sim 10^{-2}$ mm ³ /m)	Wear of alumina and 'composite' was dominated by intergranular fracture following transition to severe wear. Transition to severe wear not observed for 'nanocomposite'. Nanocomposites are more superior at higher loads.	Rodriguez et al. [130]
Al ₂ O ₃ - 15 vol.% SiC 'nanocomposite'	WC cylindrical counterface	Dry sliding wear for 10 Km at 0.24 m/s	$1-2 \times 10^{-2}$ mm ³ /N.m	Post transition wear rate of monolithic alumina is $\sim 1 \times 10^{-6}$ mm ³ /N.m, while the pre transition wear rates for monolith and nanocomposite are similar.	No transition to severe wear was observed for the nanocomposites, as against monolithic alumina. Nanocomposite containing 15 vol.% SiC was slightly superior to those having lower (5, 10 vol.%) SiC content.	Bajwa et al. [131]
Al ₂ O ₃ - 10 vol% SiC 'nanocomposite'	Oil-based suspension of 45 μ m diamond abrasive	Abrasive wear test at 350 rpm, under a constant load of 22.2 N	0.3 μ m/s (volume of material removed per unit contact area per unit time)	Wear rate of ~ 1.23 μ m/s, for monolithic alumina of similar grain size. For the nanocomposites, wear rate decreased with increase in SiC content from 2 to 10 vol.%.	Fracture mode changed from intergranular for monolithic alumina to transgranular with incorporation of nano-sized SiC particles, causing reduction in pull-out induced wear for the nanocomposites.	Ortiz-Merino and Todd [50]
Al ₂ O ₃ - 10 vol% SiC 'nanocomposite'	SiC grits of particle size 780 μ m	Wet erosive wear test at a rotation speed of 3 Hz	Fully dense ~ 1.4 nm/s; 95% dense ~ 1.8 nm/s	Fully dense monolithic alumina ~ 3.2 nm/s; 95% dense monolithic alumina ~ 7.5 nm/s	200% improvement in wear resistance for fully dense nanocomposites as compared to fully dense monolithic alumina. The improvement is $\sim 400\%$ when both the materials are $\sim 95\%$ densified.	Anyia [134]
Al ₂ O ₃ - 10 mol% TiO ₂ 'nanocomposite'	Si ₃ N ₄ balls	Pin-on-disk, with distilled water lubrication, at load of 50 N for 24 hrs, at a speed of 0.4 m/s	1×10^{-7} mm ³ /N.m	0.9×10^{-6} mm ³ /N.m for monolithic alumina	Wear of the nanocomposite shows reduced contribution from brittle fracture induced pull-out, as compared to monolithic alumina. Abrasion and plastic deformation induced wear dominates for the nanocomposites.	Lee et al. [135]
Al ₂ O ₃ - 2.5 wt.% ZrO ₂ (ZTA) nanocomposite	5 mm diameter MgO-PSZ spheres	Oscillating sliding wear at a speed of 0.15 m/s and 20 - 150 N load	$\sim 10^{-7}$ mm ³ /N.m at a load of 20 N (mild wear regime)	$\sim 10^{-6}$ mm ³ /N.m for monolithic Al ₂ O ₃ at a load of 20 N (mild wear regime)	ZTA nanocomposite possesses improved wear resistance compared to monolithic Al ₂ O ₃ in the mild wear regime (lower loads; upto 50 N), but similar wear resistance at higher loads.	Bartolome et al. [147]

2.4. Mechanical Properties of CNT Reinforced Ceramic-based Nanocomposites

By virtue of their exceptional mechanical properties such as stiffness and strength which can be as high as ~ 1 TPa and ~ 200 GPa, respectively [20,21,34,148-150], along with high aspect ratios (> 1000), ever since their discovery, carbon nanotubes have been regarded as the ultimate fibres. Such characteristics of CNTs make them potential reinforcements for the various materials classes to impart superior mechanical properties. In this light, to date various nanocomposites have been developed by incorporating CNTs into polymers [151,152], metals [7,8,19] or ceramics [19,22-24,60-66,72-78]. The effects of CNT reinforcements on the mechanical properties of different polycrystalline ceramics and ceramic glasses are summarized in Table 2.2. It must be noted that the following discussion is concerned mainly with nanocomposites in which the CNTs are randomly oriented (see section 1.1.2 of chapter 1).

2.4.1. CNT Reinforced Nanocomposites based on Polycrystalline Ceramics

Various research investigations have tried to explore the effects of CNT reinforcements on the mechanical properties of Al_2O_3 -based nanocomposites [60,61,72-76]. However, similar to the mechanical properties reported for Al_2O_3 - SiC nanocomposites, till now there is no unified consensus on the improvements achieved in the fracture toughness and strength of Al_2O_3 - CNT nanocomposites. Zhan and Mukherjee [72,73] reported that an improvement of more than three times in fracture toughness ($\sim 10 \text{ MPa m}^{1/2}$) over that of monolithic Al_2O_3 ($\sim 3.5 \text{ MPa m}^{1/2}$) is possible via incorporation of 10 vol.% SWCNT in SPS processed nanocomposites. However, such results were based on measurement of indentation crack lengths (indentation

toughness), which were later claimed to be invalid for such CNT reinforced nanocomposites by Wang and co workers [75], who demonstrated that cracking around indentations is also suppressed in the presence of only graphite particles in place of CNTs. They also reported that no increment in fracture toughness for similarly processed Al_2O_3 - SWCNT nanocomposites, with respect to pure Al_2O_3 , can be observed when the more conventional V-notch beam technique (SEVNB) is used for measuring the fracture toughness. It must be noted here that in these nanocomposites the SWCNT reinforcements were present only as ropes (bundles) along the matrix grain boundaries (see Fig. 2.10a). Based on the observations of suppression of indentation induced cracking, it was claimed that the nanocomposites possess improved contact-damage resistance with respect to pure Al_2O_3 . In a different set of investigations, the same research group also reported that the Al_2O_3 - SWCNT nanocomposites can be two orders of magnitude more creep-resistant as compared to a pure alumina of about the same grain size ($0.5\ \mu\text{m}$) [155].

In another investigation, Sun et al. [61] observed a modest improvement of 10% for the bend strength of Al_2O_3 on incorporation of just 1 wt.% MWCNT in nanocomposites developed by hot pressing. More recently, careful purification and dispersion of as received MWCNTs, followed by hot pressing, resulted in the development of Al_2O_3 - 3 vol.% MWCNT nanocomposites, with the nanotubes being present along matrix grains boundaries, as well as within the grains (see Fig. 2.10b). An increase in fracture toughness by $\sim 80\%$ (measured using Single Edge Notched Beam technique; SENB) and bend strength by $\sim 14\%$ was observed for the nanocomposites. In another work [156], which concentrated on homogeneously dispersing MWCNTs in Al_2O_3 via proper functionalization of the MWCNTs, considerably improved fracture toughness (by $\sim 25\%$; SENB) and bend strength (by $\sim$

27%) with respect to monolithic Al_2O_3 were reported for SPS processed Al_2O_3 - 0.9 vol.% MWCNT nanocomposites.

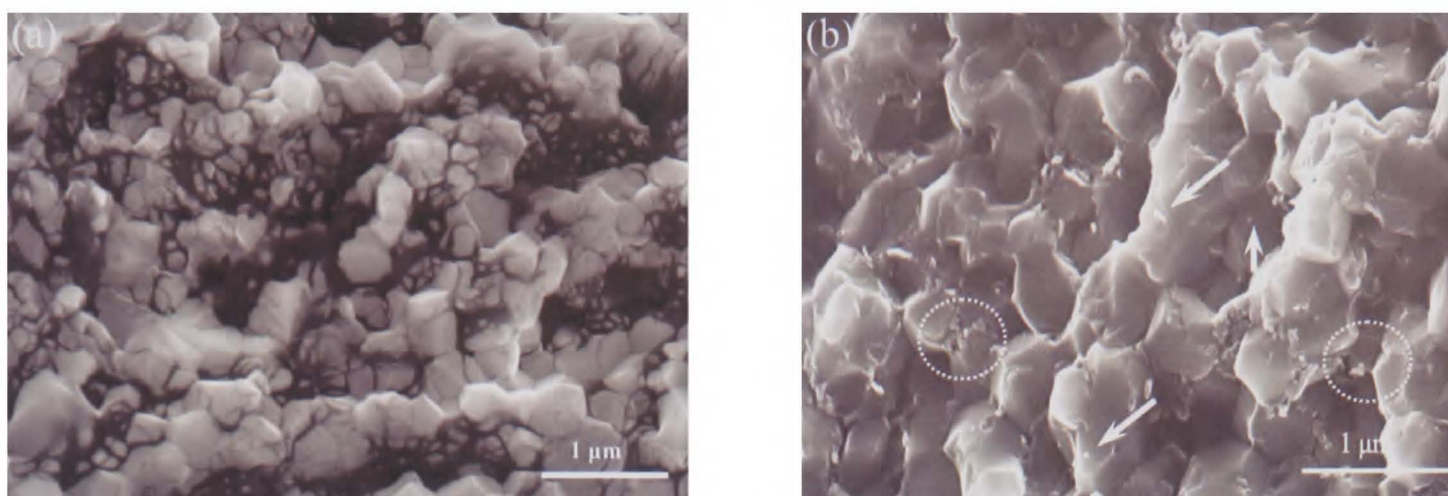


Fig. 2.10. SEM images of fractured surfaces of (a) SPS processed Al_2O_3 - 5.7 vol.% SWCNT nanocomposites containing ropes of nanotubes only along matrix grain boundaries [72]; (b) hot pressed Al_2O_3 - 3 vol.% MWCNT nanocomposites containing nanotubes along matrix grain boundaries (indicated by circles), as well as embedded within matrix grains (indicated by arrows) [60].

With respect to other polycrystalline ceramics, colloidal processing, followed by SPS resulted in the development of Si_3N_4 - SWCNT nanocomposites containing well dispersed nanotubes up to 6 vol.% [78]. A significant increase in fracture toughness (by $\sim 65\%$; measured using pre crack beam followed by 3 - point bending technique) with respect to monolithic Si_3N_4 was achieved by proper optimisation of the composition (2 vol.% SWCNT) and processing conditions (SPS; 1700°C ; 3 min). Furthermore, as compared to monolithic Si_3N_4 , the nanocomposites also possessed improved hardness and grindability.

In a significant development, Li et al. [84] developed hydroxyapatite (HAp) - 3 wt.% MWCNT nano-biocomposites via pressureless sintering in air and vacuum. The nanocomposites sintered in vacuum possessed significantly improved fracture

toughness (by $\sim 200\%$) and bend strength (by $\sim 150\%$) with respect to pure HAp. Furthermore, it was observed that the HAp - MWCNT nanocomposites possess improved histocompatibility which has significance for application as biomaterials.

2.4.2. CNT Reinforced Nanocomposites based on Ceramic Glasses

As can be seen from the previous sub-section, extensive research investigations have been carried out on CNT reinforced polycrystalline ceramics. However, comparatively little work has been done on the development and characterization of glass - CNT nanocomposites [22-24,56,65], even though earlier research results have demonstrated that considerable improvement of properties can be achieved in glasses by reinforcement with suitable carbon based fibres [157,158].

Ning et al. [56] developed SiO_2 - MWCNT nanocomposites by mixing SiO_2 powders and as received nanotubes in ethanol using magnetic stirrer and ultrasonication, followed by hot pressing. Considerable improvements in the bend strength (by $\sim 65\%$) and fracture toughness (by $\sim 100\%$; estimated by indentation crack length measurements) with respect to pure SiO_2 glass was reported for the nanocomposites containing 5 vol.% MWCNTs. However, deterioration in the mechanical properties resulted with further increase in nanotube content, which was attributed to excessive agglomeration of the MWCNTs (see Fig. 2.11a). The observed variations in the strength and fracture toughness with nanotube content are presented in Fig. 2.12a.

Another significant development with respect to fabrication of glass - CNT nanocomposites was achieved in the work of Ye and co workers [65], who reported that incorporation of 10 vol.% MWCNT resulted in improvement of the flexural strength and fracture toughness by 190% and 140% (measured using SENB),

respectively, over pure barium aluminosilicate glass/ceramic (BAS). However, similar to the SiO_2 - MWCNT nanocomposites [56], deterioration in the strength and fracture toughness was observed for MWCNT contents above 10 vol.% in the hot pressed nanocomposites (see Fig. 2.12b,c).

Considering that borosilicate glass (BSG) is one of the most important glasses with respect to technological applications, Boccaccini and co workers [23,24] tried to develop dense bulk BSG - 10 wt.% MWCNT nanocomposites via hot pressing. However, extremely poor densification (maximum of 85%) was achieved and observation of fractured surfaces of the hot pressed nanocomposites revealed that the MWCNTs were agglomerated (Fig. 2.11b). Such low densities, along with defects induced by extensive agglomeration of the MWCNTs resulted in the nanocomposite possessing poorer mechanical properties even with respect to the unreinforced BSG glass [24].

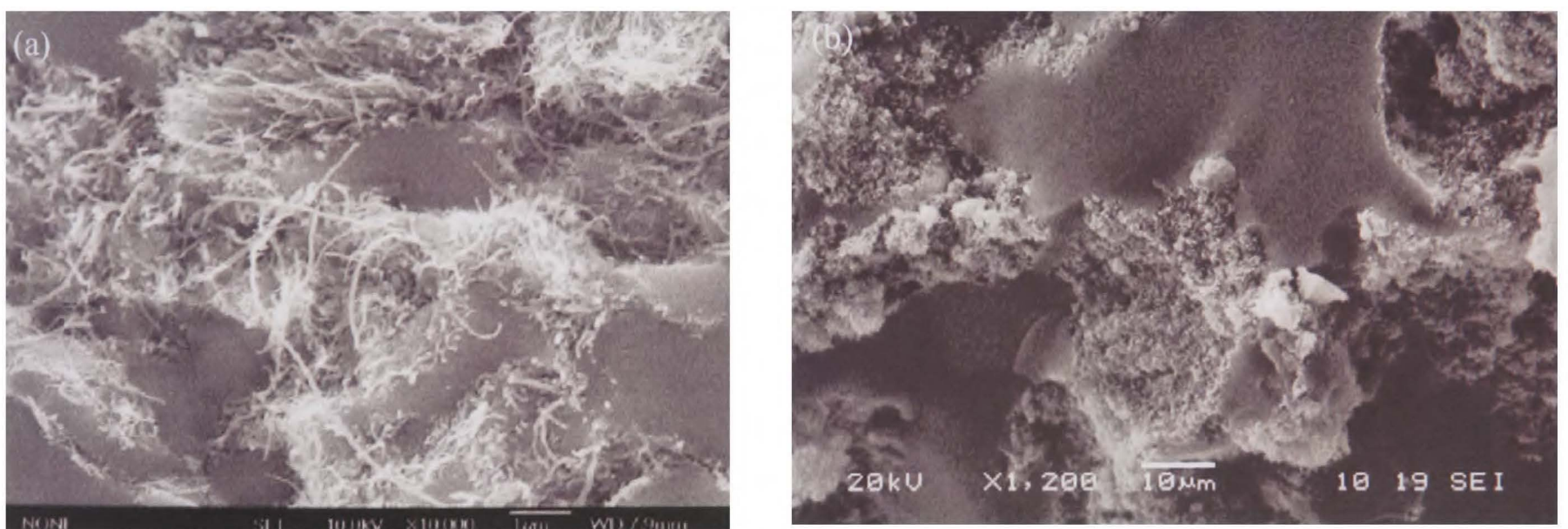


Fig. 2.11. SEM images of fractured surface showing presence of agglomerated nanotubes in hot pressed (a) SiO_2 - 10 vol.% MWCNT nanocomposite [56] and (b) BSG - 10 wt.% MWCNT nanocomposite [23].

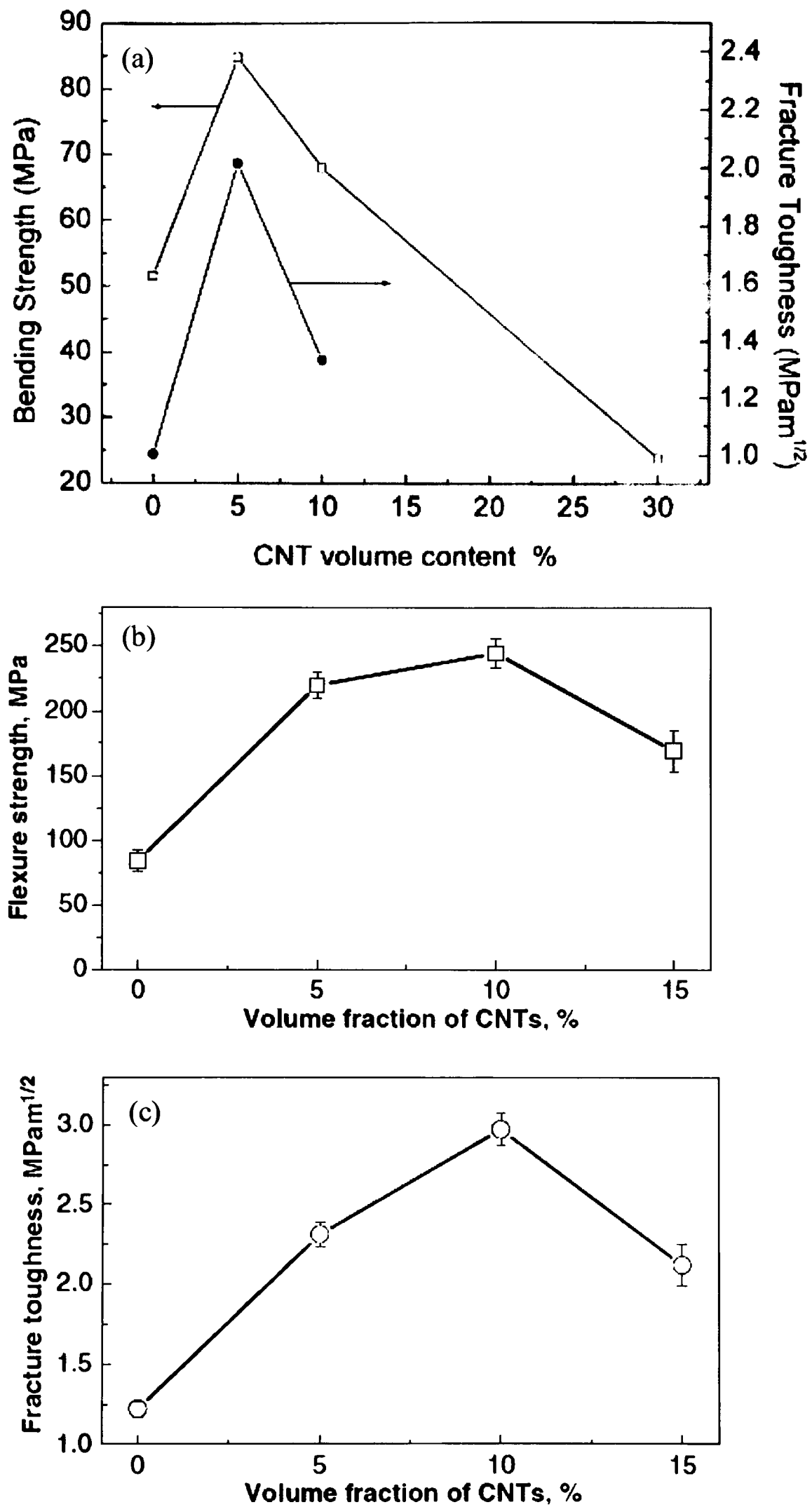


Fig. 2.12. Effects of carbon nanotube contents on the mechanical properties of (a) SiO₂ - MWCNT nanocomposites [56] and (b) BAS - MWCNT nanocomposites [65].

In a more recent work, the same research group has been able to develop dense BSG - MWCNT nanocomposites via hot pressing [62]. Sol-gel processing was used to develop the glass matrix and the nanotubes were dispersed in the sol using 3-aminopropyl triethoxysilane as binder. Good dispersion of the nanotubes were obtained for the nanocomposites containing up to 2 wt.% MWCNTs, resulting in considerable improvement in the hardness (by ~ 15%) and compressive strength (by ~ 75%) with respect to unreinforced BSG glass.

A novel processing technique, comprising careful nanotube purification and functionalization, followed by a modified sol-gel processing and subsequent hot pressing of aluminoborosilicate glass/ceramic (ABS) - CNT nanocomposites has recently been developed in our research group [22]. This processing route has allowed the development of dense nanocomposites containing well dispersed CNTs with contents up to 5 wt.%. It has also been observed that the presence of CNTs suppressed cracking around Vickers indentations.

2.4.3. Toughening Mechanisms in CNT Reinforced Ceramics

Despite considerable debate over the effects of carbon nanotube reinforcements on the mechanical properties of polycrystalline ceramics and ceramic glasses, it has now been realised that CNT additions can improve the fracture toughness of the otherwise brittle ceramic matrices. At the same time, it has also been demonstrated that careful engineering of the processing routes for achieving good dispersion of the nanotubes in the ceramic matrix, along with optimum CNT/matrix interfacial strength, is critical for retrieving the maximum possible benefits of CNT reinforcements in ceramic - CNT nanocomposites.

Xia et al. [159] carefully observed the nanoindentation induced controlled cracking at different orientations with respect to highly ordered arrays of parallel MWCNTs in an alumina matrix. Such nanocomposites were produced by growing MWCNTs via CVD (using Ni and Co as catalyst) inside arrays of well oriented open nanopores (~ 30 - 40 nm in diameter) present in alumina developed by anodising high purity aluminium. Critical analysis revealed that all the toughening mechanisms typical of conventional fibre reinforced composites, such as bridging of matrix cracks by reinforcing fibres, pull-out of the broken fibres on the fractured surfaces and crack deflection at fibre/matrix interface (see Fig. 2.13a), are operative in CNT-reinforced ceramics. It must be mentioned here that bridging of matrix cracks by reinforcing carbon nanotubes (see Fig. 2.13b), along with pull-out of the broken nanotubes on fractured surfaces (see Fig. 2.13c), have been regularly observed for different CNT reinforced nanocomposites based on polycrystalline ceramics as well as ceramic glasses. Such bridging by the nanotubes restrains the crack from opening and reduces the driving force for crack propagation in the matrix [159,160-164]. Energy is consumed as elastic strain energy stored in the bridging fibres getting stretched with increase in the crack opening [159,160-164]. Additionally, energy is dissipated in the form of the work required to pull the embedded broken fibres out against any residual frictional stresses at the fibre/matrix interface [159,160,162-165].

In the study by Xia et al. [159] it was also observed that deformation around indentations can be accommodated by lateral buckling or collapse of the nanotubes in shear bands. Such nanotube collapse in shear bands virtually prevents propagation of cracks emanating from indentation corners (see Fig. 2.13d). It must be recalled here that other groups have also reported suppression of cracking around Vickers indentations for alumina - CNT [72,73,75] and ABS - CNT [21,161] nanocomposites,

as compared to the unreinforced matrices. Such observations suggest that that ceramic - CNT nanocomposites can possess multiaxial damage tolerance against contact loading.

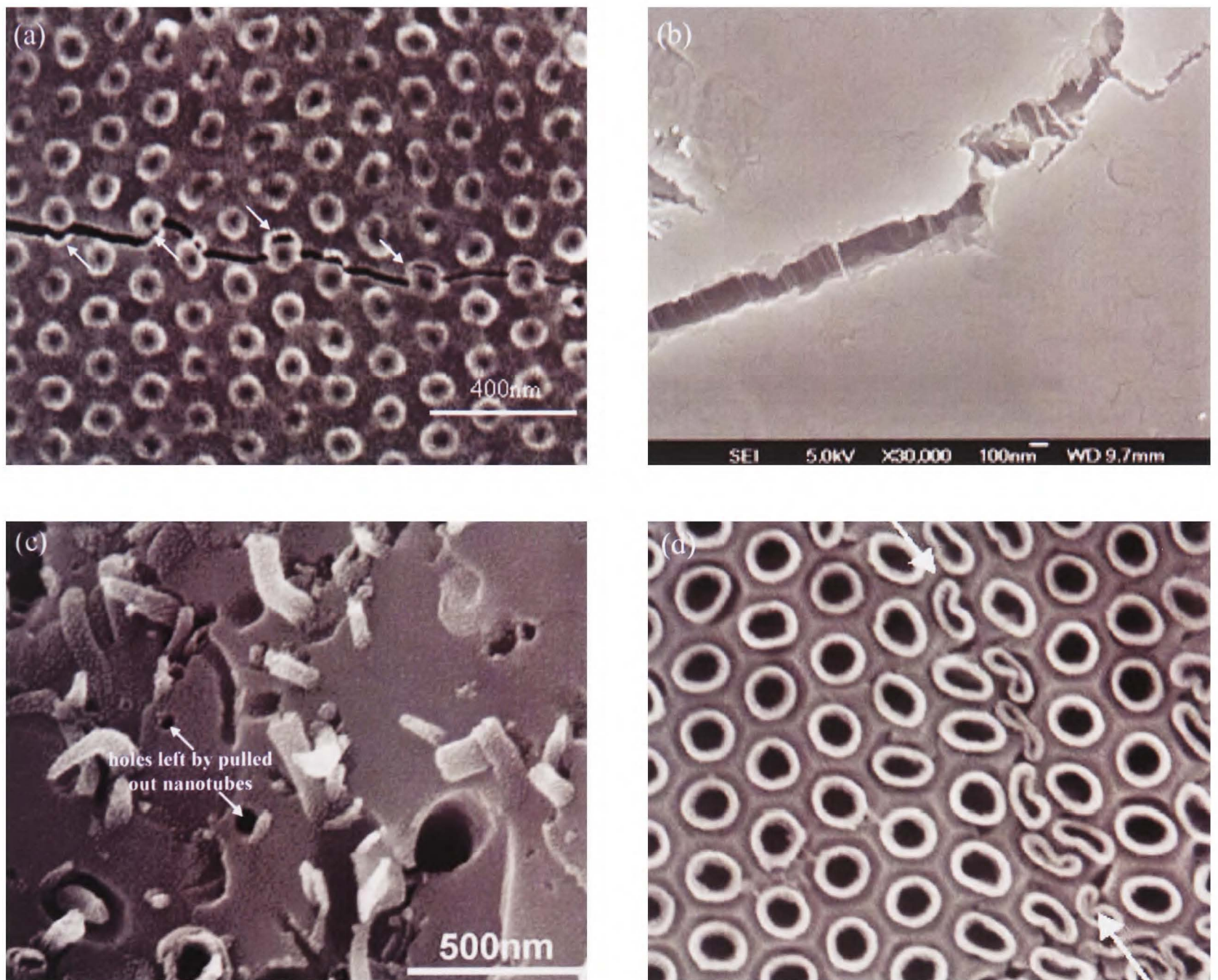


Fig. 2.13. SEM images providing evidences of toughening mechanisms operating in ceramic - CNT nanocomposites. (a) crack deflection at matrix/CNT interface in ordered Al_2O_3 - MWCNT nanocomposites [159]; (b) crack bridging by nanotubes in ABS - 5 wt.% MWCNT nanocomposite [21]; (c) pulled out nanotubes, along with residual holes, on the fracture surface of ABS - 5 vol.% SWCNT nanocomposite [65]; (d) nanotube collapse in shear bands observed around nano indentations on ordered Al_2O_3 - MWCNT nanocomposites [159].

Table 2.2. Effects of CNT reinforcements on the mechanical properties of various nanocomposites based on polycrystalline ceramics and ceramic glasses. [Processing routes are abbreviated as: SPS = spark plasma sintering; HP = hot pressing; PS = pressureless sintering; Methods of fracture toughness measurements are abbreviated as: VI = measurement of crack lengths around Vickers Indentation; SEVNB = single edge V-notch beam; SENB = single edge notch beam]

ceramic polycrystals / glass matrix	CNT reinforcements	sintering technique	improvement in mechanical properties (%) with respect to matrix		method used for fracture toughness measurement	references
			fracture toughness	flexural strength		
Al ₂ O ₃	5.7 vol.% SWCNT	SPS	140%	-	VI	Zhan et al. [72,73]
	10 vol.% SWCNT		194	-		
	10 vol.% SWCNT	SPS	negligible	-	SEVNB	Wang et al. [75]
	10 wt.% MWCNT	HP	negligible	10%	VI	Sun et al. [61]
	1 vol.% MWCNT	SPS	40%	-	VI	Cha et al. [76]
	0.9 vol.% MWCNT	SPS	25%	27%	SENB	Yamamoto et al. [156]
	3 vol.% MWCNT	HP	80%	13%	SENB	Wei et al. [60]
Si ₃ N ₄	1 vol.% SWCNT	SPS	47.2%	-	pre crack beam followed by 3 - point bending technique	Corral et al. [78]
	2 vol.% SWCNT		65%	-		
	6 vol.% SWCNT		37%	-		
HAp	3 wt.% MWCNT	PS	200%	150%	SENB	Li et al. [84]
BSG glass	10 wt.% MWCNT	HP	11%	- 40% (decrease)	SENB	Boccaccini et al. [24]
SiO ₂ glass	5 vol.% MWCNT	HP	100%	65%	VI	Ning et al. [56]
	10 vol.% MWCNT		30%	30%		
BAS glass	5 vol.% MWCNT	HP	90%	162%	SENB	Ye et al. [65]
	10 vol.% MWCNT		140%	190%		
	15 vol.% MWCNT		74%	102%		

2.5. Thermal and Electrical Conductivities of Ceramic - CNT Nanocomposites

In addition to the exceptional mechanical properties, carbon nanotubes have been reported to possess very high electrical and thermal conductivities, which are superior to even the most conductive of materials known [20,166-169]. Experimental results show that SWCNT rope has an electrical conductivity of $\sim 10^4$ S/cm at room temperature along the longitudinal direction [20,168,169]. Also, MWCNTs are reported to possess an electrical conductivity of $\sim 1.9 \times 10^3$ S/cm [166]. With regard to thermal properties, room temperature thermal conductivities of ~ 200 W/mK for bulk samples of SWCNTs [171] and ~ 3000 W/mK for individual MWCNTs [167,170,171] have been reported based on experimental measurements. It is believed that owing to their high aspect ratios and high specific surface areas, carbon nanotubes can form conductive paths at relatively low contents in CNT reinforced ceramic nanocomposites, which can result in considerable improvement in the conductivities of the insulating ceramic materials.

Rul and co workers reported for the first time percolation of carbon nanotubes in an electrically insulating spinel (MgAl_2O_4) matrix [172]. As little as 0.64 vol.% of SWCNTs was enough to achieve an interconnected network of insulating path through the nanocomposite (percolation), resulting in a seven orders of magnitude (from 10^{-10} for the matrix spinel to 4×10^{-3} S/cm for the nanocomposite) jump in the electrical conductivity at the threshold (p_c). It was observed that up to a nanotube content of 11 vol.% the DC electrical conductivity (σ) fitted well with the scaling law of the percolation theory [$\sigma = k(\rho - \rho_c)^t$] (see Fig. 2.14a). A maximum electrical conductivity of 8.5 S/cm was recorded for the nanocomposite containing 25 vol.% SWCNTs.

Similar percolation behaviour, with a low percolation threshold of ~ 1.7 wt.% MWCNT, was also observed for 3Y-TZP (3 mol.% yttria stabilized tetragonal ZrO_2 polycrystals) - MWCNT nanocomposites [173]. The electrical conductivity increased with nanotube content beyond p_c to reach a maximum of $\sim 7.4 \times 10^{-2}$ S/cm on reinforcement with 10 wt.% MWCNTs, as compared to $\sim 6 \times 10^{-6}$ S/cm for unreinforced 3Y-TZP. Furthermore, it was also observed that the dielectric constant increased significantly with the MWCNT content being near to the percolation threshold.

In probably one of the more significant achievements with regard to the electrical conductivities of ceramic - CNT nanocomposites, Zhan et al. [73,174] observed an increase by 12 orders of magnitude in the electrical conductivity of Al_2O_3 ($\sim 10^{-11}$ S/cm) on reinforcement with 15 vol.% SWCNT (~ 33.45 S/cm for the nanocomposite). Such conductivity approaches the metallic conduction threshold of $\sim 10^2$ S/cm [73,175]. However, no improvement in the thermal diffusivities was observed for the nanocomposites over that of unreinforced alumina [73]. In a more recent work, a percolation threshold of ~ 0.8 vol.% MWCNT was observed in Al_2O_3 - MWCNT nanocomposites, resulting in an increase in electrical conductivity by 10^8 orders of magnitude (to $\sim 9 \times 10^{-2}$ S/cm), with respect to unreinforced alumina ($\sim 5 \times 10^{-10}$ S/cm) [176].

In contrast to these reports, Huang and Gao observed that the electrical conductivity of BaTiO_3 - MWCNT nanocomposites decreased steadily with MWCNT content (up to 3 wt.%) [177]. On a different note, the BaTiO_3 semiconductor transformed from n-type to p-type on incorporation of carbon nanotubes. These observations were attributed to the formation of Schottky barrier at the matrix/MWCNT interfaces. In a separate work, the same research group observed that, as opposed to the usually

observed slower densification kinetics for carbon nanotube containing composites [22-24,55,56], incorporation of MWCNT accelerated the densification kinetics of BaTiO₃ - MWCNT nanocomposites when sintered using SPS technique [170]. The excellent electrical and thermal conductivity of MWCNTs were believed to be responsible for such unexpected sintering behaviour. However, similar to the electrical conductivity [170], the thermal diffusivity and conductivity of BaTiO₃ were observed to decrease with increase in MWCNT content. Interfacial thermal barrier between the MWCNTs and the BaTiO₃ matrix was believed to be responsible for the adverse effect on the thermal conductivity.

As with the mechanical properties, very few reports are available on the effects of carbon nanotube reinforcements on thermal and electrical conductivities of ceramic glasses [24,62,178]. In this regard, Sivakumar et al. [178] observed modest increments in thermal conductivity of SiO₂ glass on reinforcement with MWCNT. A maximum conductivity of 4.08 W m⁻¹ K⁻¹ was measured for the nanocomposite containing 10 vol.% MWCNTs. As compared with a thermal conductivity of ~ 2.5 W m⁻¹ K⁻¹ for pure SiO₂ glass, such a modest increment was found to be well below the theoretical prediction. It was demonstrated that high resistance at the nanotube/matrix or nanotube/nanotube interfaces limits thermal transport along percolating networks of CNTs, which implies that the properties of the interfaces are critical towards utilizing the excellent thermal conductivity of carbon nanotubes in CNT reinforced nanocomposites.

In one of the pioneering works concerning the development of borosilicate glass (BSG) - CNT nanocomposites, Boccaccini et al. [24] observed that, even though poor dispersion of the MWCNTs and lower densification prevented any improvement in the mechanical properties, the electrical conductivity of the BSG - 10 wt.% MWCNT

nanocomposite ($\sim 8 \times 10^{-2}$ S/cm) was three orders of magnitude higher than that of the unreinforced BSG glass ($\sim 10^{-5}$ S/cm) (Fig. 2.14b). In a more recent work, the same research group observed percolation effects in BSG - MWCNT nanocomposites, containing well dispersed nanotubes (up to 3 wt.%) [62]. The percolation threshold was estimated to be at ~ 1.75 wt.% MWCNT. However, only modest improvements in the thermal conductivity was observed with MWCNT additions up to 2 wt.%.

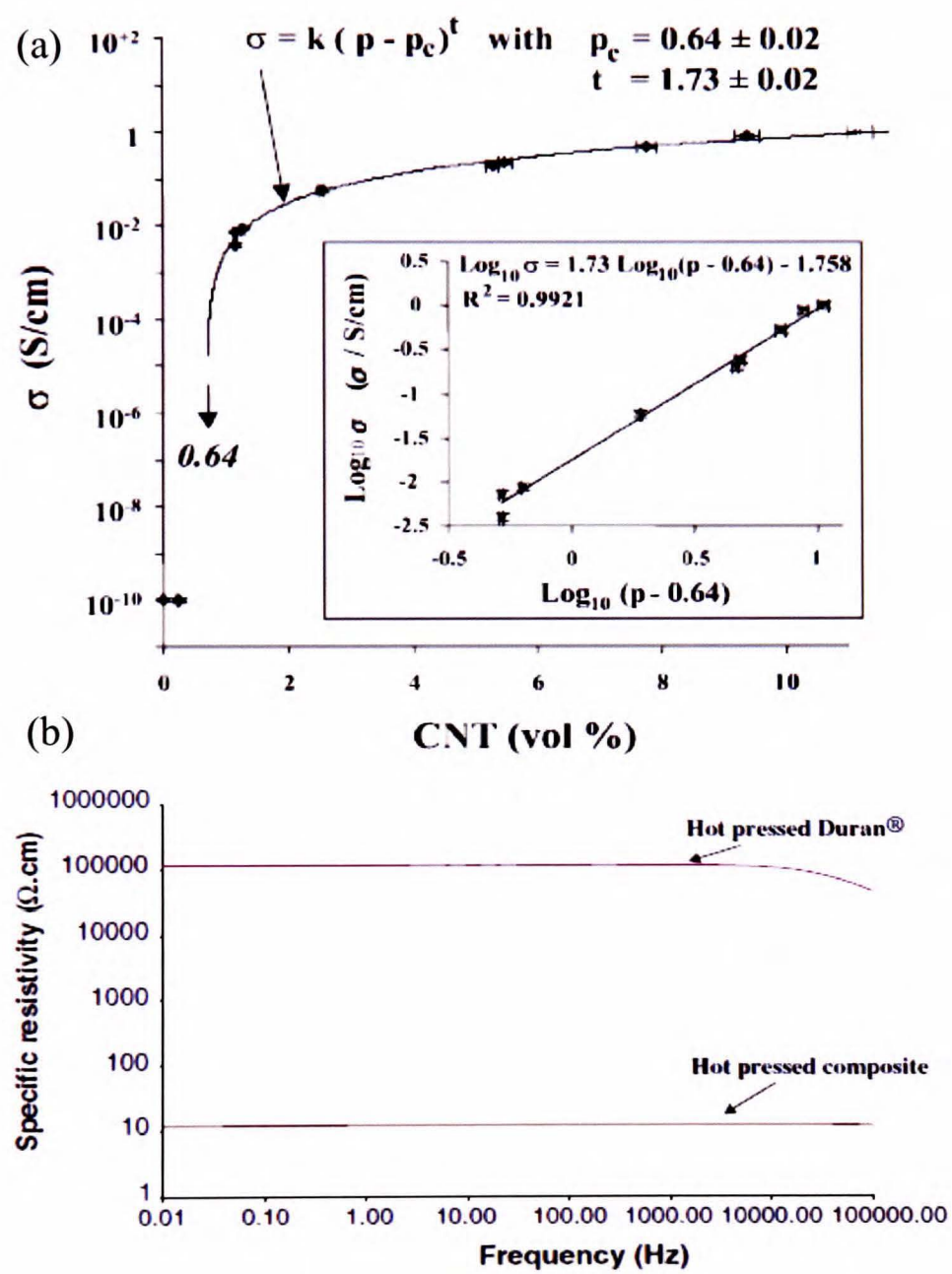


Fig. 2.14. (a) Percolation effects of carbon nanotube on the electrical conductivity of MgAl_2O_4 - SWCNT nanocomposites demonstrated using a plot of electrical conductivity (σ) as a function of the CNT content (p) [172]. Note the jump of seven orders of magnitude in σ at the percolation threshold (p_c) of 0.64 vol.% SWCNT. (b) 10^5 times higher specific electrical resistivity ($1/\text{conductivity}$) values of unreinforced borosilicate ‘Duran’ glass (BSG) as compared to BSG - 10 wt.% MWCNT nanocomposite [24].

2.6. Objectives of the Present Research

As has been discussed in the preceding sections, ceramic-based nanocomposites, both particulate as well as carbon nanotube reinforced, possess significantly improved properties with respect to the unreinforced conventional ceramics. However, various issues still need to be addressed in order to make such materials viable for extensive use in the commercial field. Broadly, such issues are concerned with the processing related problems as well as a persisting lack of complete understanding and exploration of the various properties of the different ceramic-based nanocomposites.

2.6.1. Particulate Reinforced Alumina-based Nanocomposites

In the light of the problems pertaining to the development of particulate ceramic nanocomposites via powder metallurgical routes, one of the possible but virtually unexplored routes to develop such nanocomposites is via in-situ formation of nano-sized particles. Hence, in this work, we aim to design a novel and commercially feasible processing route, by adapting an idea routinely used in age-hardened metals, to develop ceramic “nanocomposites” by solid state precipitation during aging of supersaturated solid solutions. Fe_2O_3 (haematite) belonging to the same space group ($R\bar{3}c$) as $\alpha\text{-Al}_2\text{O}_3$ (corundum) possesses substantial solubility in Al_2O_3 at moderately high temperatures in air (~ 15 wt.% at $\sim 1410^\circ\text{C}$) [179]. Under reducing conditions Fe^{3+} (of dissolved Fe_2O_3) can be reduced to Fe^{2+} , which being aliovalent to Al^{3+} possess negligible solubility in Al_2O_3 . Hence, it is expected that aging of ‘supersaturated’ Al_2O_3 - Fe_2O_3 solid solutions under reducing conditions may lead to the formation of Fe^{2+} containing precipitate particles.

Development of Al_2O_3 -based nanocomposites via this technique would solve the following problems associated with the processing of particulate reinforced ceramic-based nanocomposites:

- a) Uniformly dispersed nanosized second phase particles can be produced in the as sintered bulk nanocomposite without the requirement of ultra fine sized starting powders ($< \sim 50 \text{ nm}$) which are very expensive and require special care during subsequent processing.
- b) Near theoretical densification can be attained using cheaper and commercially friendly pressureless sintering technique, thus further reducing processing cost significantly and at the same time allowing the development of products of different shapes/sizes through continuous batch production process.
- c) Through careful design of the heat treatment schedules the technique provides the feasibility of producing second phase particles of varying sizes, distribution and amount, based on their effects on the material properties required for different applications.
- d) Overall production of ceramic nanocomposites, possessing improved mechanical and tribological properties, via such a technique is believed to address the issues that hitherto have hindered commercial applicability of such promising materials.

In this perspective, some salient objectives can be precisely presented as follows:

- To investigate the feasibility of developing Al_2O_3 -based nanocomposites via dissolution of 10 wt.% Fe_2O_3 in Al_2O_3 during pressureless sintering in air and subsequent aging of the dense solid solutions in reducing atmosphere (forming gas; $\text{N}_2 + 4\% \text{ H}_2$).

- Through in detail investigation of the phase content and microstructural developments, as functions of the aging schedules, this work further aims to examine the extent to which a uniform dispersion of nanosized particles can be produced by optimising the processing conditions.
- Careful planning of the aging treatments at various temperatures (1250°C - 1550°C) for different durations (upto 50 h), along with critical analysis of the phase/microstructural developments, is intended to allow us to gain an insight into the micro-mechanisms governing such precipitation route.
- To investigate and understand the effects of the precipitation of Fe^{2+} containing second phase particles on the mechanical and tribological properties of the as developed nanocomposites. This is expected to allow for further optimization of the processing schedule performed based on the observed changes in the material properties, as well as giving insight into the mechanisms resulting in improved properties in alumina-matrix nanocomposites.

2.6.2. Carbon Nanotube Reinforced Aluminoborosilicate Glass based Nanocomposite

The inability to disperse carbon nanotubes in various polycrystalline ceramics and glass-based matrices, accompanied by poor sintered densities of the ceramic - CNT nanocomposites, has been the major hindrance towards utilizing the exceptional properties of CNTs for developing nanocomposites possessing significantly improved properties [19-21,23,24]. In order to address this issue, recently in our group a novel route comprising careful purification/functionalization of the pristine MWCNTs,

followed by ultrasonication assisted sol-gel processing and hot pressing, has been developed which allows the development of dense aluminoborosilicate glass (ABS) - CNT nanocomposites containing well dispersed CNTs up to 5 wt.% [22]. However, the maximum amount of CNTs that can be homogeneously dispersed using this process, along with the possible improvements in the mechanical, thermal and electrical properties that can be achieved for the dense ABS - CNT nanocomposites, is yet to be established. Additionally, still lacking is a scientific understanding of the reinforcing mechanisms leading to such improvements. Although single walled nanotubes (SWCNT) are in principle more favourable as reinforcements for improving mechanical properties of nanocomposites, in the present investigation MWCNT has been used because their lower costs make them more suitable for commercial applications.

In this perspective, some salient objectives can be precisely presented as follows:

- Following on from the previous work, this research tries to explore the feasibility of achieving homogeneous dispersion of higher amounts of MWCNT (up to 15 wt.%) in ABS matrix and at the same time develop dense ABS - MWCNT nanocomposites using similar processing route.
- Another major objective is to investigate the effects of the different amounts of MWCNT reinforcements on the mechanical properties of these nanocomposites. It also aims at critically analyzing the contributions of different toughening mechanisms towards possible improvements in the properties at the optimum MWCNT contents. Such scientific understanding is believed to throw light on the avenues for further improving the mechanical properties of CNT reinforced nanocomposites.

- Considering that reinforcement by carbon nanotubes might lead to improvements in the electrical and thermal conductivities, and that such improvements might open up new vistas for applications of borosilicate glass in various electronic industries, this research also aims to investigate and understand the electrical and thermal properties of the ABS - MWCNT nanocomposites as functions of the nanotube content.

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Chapter 3

EXPERIMENTAL DETAILS

3.1. Development of the Particulate and MWCNT Reinforced Nanocomposites

3.1.1. Al₂O₃-based Particulate Nanocomposites

3.1.1.1. Synthesis of Al₂O₃ - Fe₂O₃ Powders

High purity (~ 99.995%), fine (particle size ~ 200 nm) α -Al₂O₃ powders (AKP50, Sumitomo, Japan) were used as the starting material for the matrix (Al₂O₃). In order to prevent abnormal grain growth during sintering and to enable near theoretical densification, the Al₂O₃ powders were doped with 250 ppm (by weight) of MgO using pure MgO powders (99.95 %; 120 nm; UBE, Japan) [1]. The MgO doped Al₂O₃ powders were dispersed in ethanol using an ultrasonic probe. The incorporation of Fe³⁺ was achieved by adding a solution of Fe(NO₃)₃.9H₂O (Sigma Aldrich, UK, purity > 98%) in ethanol to the alumina slurries. The Fe(NO₃)₃ solutions contained the requisite amount of the salt that would result in doping levels corresponding to 10 wt.% Fe₂O₃ in Al₂O₃. In order to study the effects of small amounts of Y₂O₃ addition (250 ppm by weight) on the microstructural developments, the requisite amounts of Y(NO₃)₃.6H₂O dissolved in ethanol were also added to some of the slurries. Since Fe(NO₃)₃.9H₂O and Y(NO₃)₃.6H₂O are completely soluble in ethanol, the addition of such solution is expected to result in a homogeneous distribution of Fe³⁺ and Y³⁺ in the alumina slurries. Some pure alumina slurries were also made for comparison. All the slurries were ball milled for 24 hours in bottles made of polyethylene, using high purity (99.99%) alumina balls. After ball milling the slurries were dried on a hot plate with constant stirring, using a magnetic stirrer, to prevent segregation. The dried powders were lightly crushed to remove agglomerates, gently ground in an Al₂O₃ mortar and pestle and passed through a 150 μ m sieve.

It must be mentioned here that high purity Al₂O₃ powders have been used in the present work for aiding scientific study, that is to eliminate any possible effects of

other minor constituents, such work can be carried out industrially using commercial grades of powders. Additionally, since freeze drying of water based slurries was not possible due to the presence of an excess amount of dissolved salt, ethanol was used as dispersing medium. However, for commercial production water can be used as the dispersing medium since $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, as well as $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, gets dissolved in water as well. The subsequent drying can be achieved using spray drying, which should prevent agglomeration.

3.1.1.2. Sintering and Solution Treatment

Green compacts were produced by uniaxial cold pressing of the powders into 20 mm discs at 100 MPa. The first step in the present processing scheme involved sintering to near theoretical densities for the pure Al_2O_3 and Fe-containing Al_2O_3 pellets. The green compacts were densified using pressureless sintering in air inside an alumina tube furnace (Lenton, UK). The as sintered pellets were around 3 mm thick. The Al_2O_3 samples containing 10 wt.% Fe_2O_3 will henceforth be referred to as 'A10F' and the samples additionally doped with Y_2O_3 (250 ppm) will be referred to as A10FY. During the sintering cycle, the A10F green pellets were slowly heated at $5^\circ\text{C}/\text{min}$ up to a temperature of 750°C and held there for 1 hour in order to decompose the ferric nitrate to Fe_2O_3 . Following this, a heating rate of $10^\circ\text{C}/\text{min}$ was used up to the sintering temperature of 1450°C . The pure Al_2O_3 pellets were directly heated to the sintering temperature of 1450°C from room temperature at a heating rate of $10^\circ\text{C}/\text{min}$. The selected sintering temperature of 1450°C corresponds to the temperature on the Al_2O_3 - Fe_2O_3 phase diagram, where ~ 15 wt.% Fe_2O_3 is soluble in Al_2O_3 (Fig. 3.1) [2]. Hence it is expected that all of the Fe_2O_3 in the A10F specimens will be dissolved in the Al_2O_3 during sintering to yield an alumina-based solid solution containing Fe^{3+} .

cations. In this perspective, the sintering step is designed to solve the dual purpose of attaining densification and developing Al_2O_3 - 10 wt.% Fe_2O_3 (A10F) solid solutions. To ensure complete dissolution and homogeneous distribution of Fe^{3+} in the cation sub-lattice of Al_2O_3 , the samples were held at the sintering temperature (1450°C) for 5 hrs (solution treatment). After completion of the solution treatment, in order to avoid possible segregation of the dissolved Fe along matrix grain boundaries or even precipitation of Fe_2O_3 during furnace cooling, the samples were ‘quenched’ by pushing them immediately to the end of the furnace tube using an alumina rod, where the temperature is expected to be $\sim 100^\circ\text{C}$. A schematic representation of the quenching step is presented in Fig. 3.2.

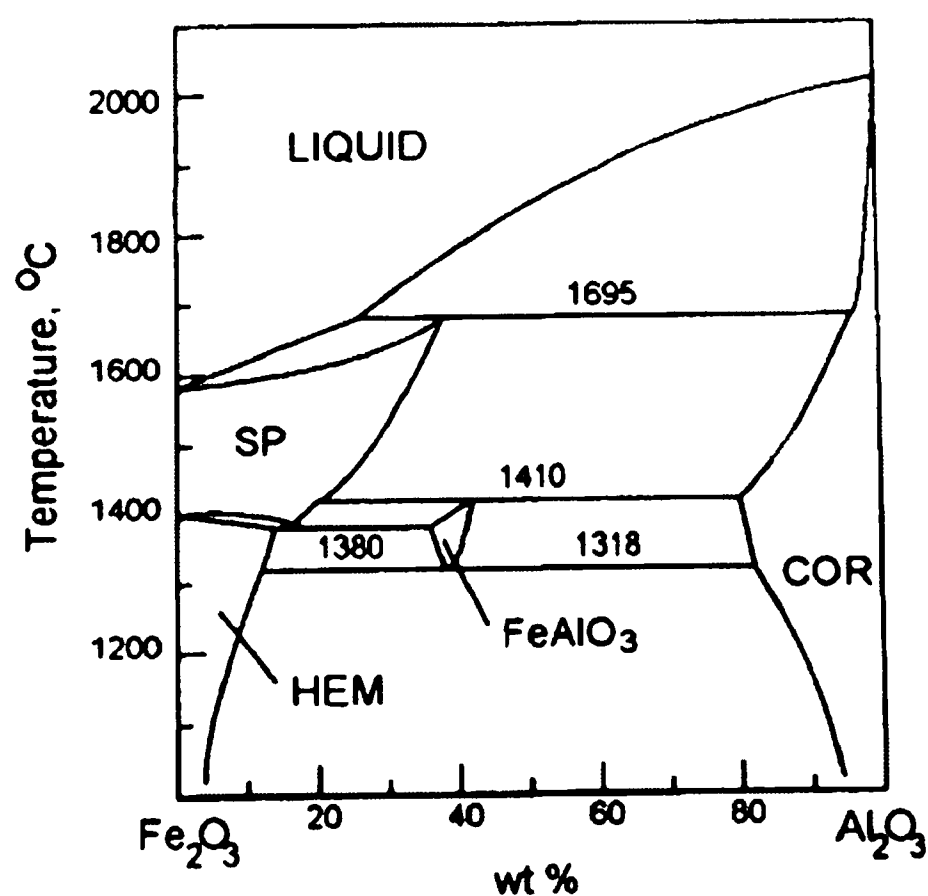


Fig. 3.1. Quasibinary phase diagram of the $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3$ system in air. COR: corundum (Al_2O_3); HEM: hematite (Fe_2O_3); and SP: spinel [2].

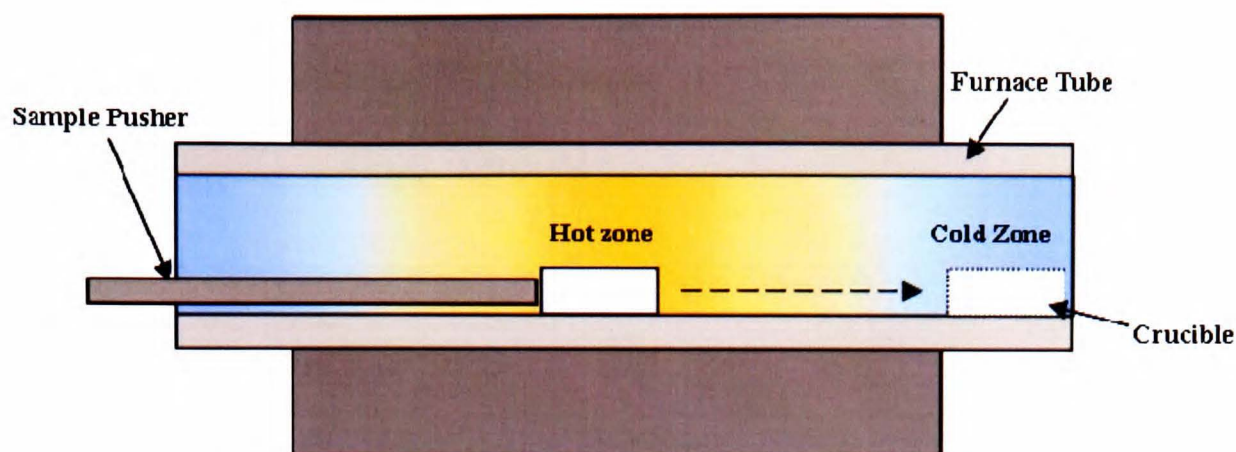


Fig. 3.2. Schematic representation of the arrangement used for quenching the samples out of the furnace hot zone after completion of sintering/solution treatment.

3.1.1.3. Aging Treatment

In order to develop the nanocomposites, the second major step in the heat treatment scheme was the generation of Fe-containing second phase particles during heat treatment of the densified Al_2O_3 - 10 wt.% Fe_2O_3 solid solutions. Since, as compared to Fe^{3+} there is negligible solubility for Fe^{2+} in Al_2O_3 [3,4], the 'supersaturated' solid solutions were aged under reducing conditions using a N_2 - 4% H_2 forming gas mixture in an alumina tube furnace (Lenton, UK) having ends sealed by caps. A gas flow rate of $200 \text{ cm}^3/\text{min}$ was used. In order to optimize the aging schedules for development of the Al_2O_3 -based particulate nanocomposites, the heat treatments were performed at different temperatures (1250°C - 1550°C) and for different durations up to 50 h. A heating and cooling rate of $10^\circ\text{C}/\text{min}$ was used for the aging treatments.

3.1.2. Aluminoborosilicate - Multi Walled Carbon Nanotube Nanocomposites

3.1.2.1. Carbon Nanotube Purification and Functionalization

The first step in the processing scheme for developing the multi walled carbon nanotube (MWCNT) reinforced aluminoborosilicate (ABS) glass/ceramic

nanocomposites involved careful purification and side wall functionalization of the as received CVD grown pristine MWCNTs (supplied by Thomas SWAN & Co. Ltd, UK). In order to remove the amorphous carbon and other graphitic particles present in such CVD grown nanotubes [5-7] they were subjected to steam purification at 900°C for 4 hrs. Such steam purification schedule has been developed in the Oxford Nanotube Group [5] and successfully applied earlier to purify such nanotubes [5-7]. The steam purification step is essential also for the efficient sidewall functionalization of carbon nanotubes [6]. The purified MWCNTs were then subjected to nitric acid (9 M) refluxing at 100°C for 24 hrs in order to carboxylate the carbon nanotube walls and remove catalytic metal particles [7,8]. This was followed by ultrasonication (W-375, Heat-Systems Ultrasonic, Inc) for 2 h in 450 mL of 8:1 (v:v) NH₄OH-ethanol solution for partial esterification of the carboxylic acid groups [7]. Finally the functionalized MWCNTs were filtered through a 200 nm polycarbonate membrane repeatedly to remove ammonia completely and then re-dispersed in ethanol using ultrasonication.

3.1.2.2. Nanocomposite Development via Sol-Gel Processing and Hot Pressing

The MWCNT containing ABS nanocomposite powders was made via modification of a previously reported sol-gel processing method [9]. The different constituents were homogeneously mixed and dispersed via sonication using an ultrasonic probe operating at 300 kHz. Suspensions were maintained approximately at 50°C during sonication. The precursors used in the present sol-gel processing are Tetraethoxysilane (TEOS, Aldrich, >98%), aluminium sec-butoxide (Aldrich, >98%), trimethyl borate (TMB, Aldrich, >98%), and sodium acetate (BDH, England, 99%).

Initially 38 mL of TEOS, 38 mL of ethanol and 3.8 mL of distilled water were mixed together, followed by the addition of 0.5 mL of concentrated HCl as a catalyst. The resulting mixture was sonicated until the suspension became a clear colourless liquid, when 5.4 mL of TMB was added which was followed by ultrasonication for another 5 min. 18 mL of aluminium sec-butoxide was then added and the suspension was sonicated for another 5 min. In order to obtain nanocomposites containing x wt.%, MWCNTs (x = 2.5, 5, 10 and 15) corresponding amounts of functionalized MWNTs in ethanol suspensions were incorporated into the sol. The MWCNT containing glass sols were sonicated for 10 min to allow homogeneous dispersion of the nanotubes. Finally, 8 mL of 2 M sodium acetate solution was added to the sol, which was then sonicated until gelation.

The gel was then dried in an oven and the as-prepared ABS - MWCNT powders were ground with a powder grinder at 60 rpm and sieved to 150 μm . The powders were then calcined at 350°C in air for 4 h in order to remove organic residues. Subsequently, the nanocomposite powders containing 0 - 15 wt% MWCNT were hot pressed in a 15 mm graphite die under a maximum pressure of 25 MPa in argon atmosphere. A heating rate of 30°C/min was used up to the hot pressing temperature of 950°C where the samples were held for 2 h, following which the pressure was released and the power turned off to allow furnace cooling. A flow chart representing an overview of the present processing scheme is presented in Fig. 3.3.

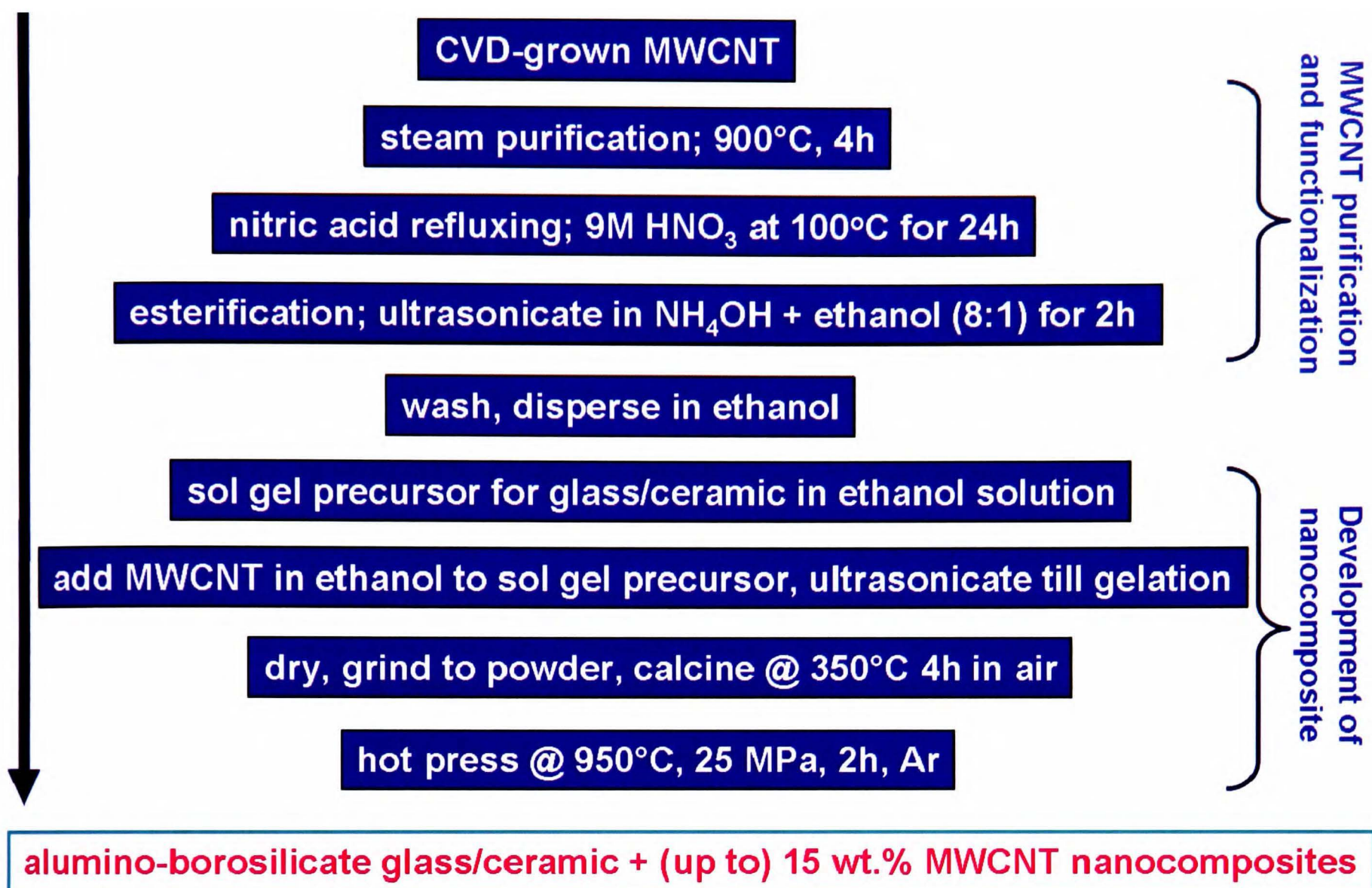


Fig. 3.3. Overview of the processing scheme used to produce bulk ABS - MWCNT nanocomposites via sol-gel processing and subsequent hot pressing.

3.2. Investigation of Phase Evolution and Microstructural Development

The sintered densities of all the particulate and MWCNT reinforced nanocomposites, as well as monolithic Al₂O₃ and ABS glass/ceramic, were measured in distilled water according to Archimedes' principle. For the phase identification and microstructural characterizations all the samples were ground and polished using 25, 6, 3, 1 and 0.25 μm diamond slurries in order to remove the external surfaces and produce optically reflective ceramographic surfaces representative of the sample cores. Furthermore, the

Al₂O₃-based samples were also cut along a diameter and polished to observe the microstructural development along the cross sections. Polishing of all the samples was performed using a Buehler Motopol 2000 and Logitech PM2 automatic lapping and polishing machines.

The phase identifications were performed by X-ray diffraction (XRD) in a θ -2 θ diffractometer (Philips, Netherlands) at a collection rate of 3°/min using CuK α radiation. For the Al₂O₃-based samples, further investigation involved estimation of the change in interplanar spacings of the matrix due to solution and aging treatments. Such estimation was made by measuring the shifts of the (113) and (226) Al₂O₃ peak positions in the XRD patterns. An extrapolation procedure [10] was used to obtain accurate values of interplanar spacings by plotting the calculated values of d_{113} for each peak against $\cos^2\theta/\sin\theta$ and extrapolating the lines joining the points to $\cos^2\theta/\sin\theta = 0$.

The microstructures of the as polished surfaces were extensively observed for the Al₂O₃-based samples. In order to reveal the grain boundaries of the as sintered pure Al₂O₃ and A10F solid solution samples, thermal etching was done at a temperature of 1400°C for 15 min in air. Following thermal etching, the samples were again ‘quenched’ in the manner described earlier (see section 3.1.1.2). The microstructures were observed using a field emission SEM (JEOL 6500F) operated at 20 kV. Elemental analysis was performed using Energy Dispersive Spectroscopy (EDS), attached to the SEM. Volume fractions of the second phase particles were determined via point counting on back scattered electron (BSE) images and the average particle sizes were determined from the mean of the major and minor axes of at least 20 particles, multiplied by 1.27 to obtain equivalent spherical diameters [11].

The fractured surfaces of the Al_2O_3 -based samples and the ABS-based samples, as well as the Vickers indentations obtained on the polished surfaces, were also studied in detail. Such observations were made using the same FEG SEM (JEOL 6500F), which was operated at 20 kV for the Al_2O_3 -based samples and at 5 kV for the ABS-based samples. For avoiding charging during SEM observations, all specimens of the Al_2O_3 -based samples were sputter coated with carbon and the ABS-based samples were coated with platinum. Furthermore, the fractured surfaces of the ABS - MWCNT nanocomposites were also characterized in detail using atomic force microscopy (AFM).

Sample preparation for transmission electron microscope (TEM) observations involved mechanical thinning of 3 mm discs, followed by ion-milling to electron transparency in a Gatan Duo Mill (5 kV). Observations were performed using 200 kV JEOL 2000FX and Philips CM20 TEMs, equipped with EDS systems. More detailed investigations for the ABS-MWCNT nanocomposites were performed using high resolution transmission electron microscopy HRTEM (JEOL 4000EX) operated at 300 kV. The author would like to thank Prof. John Hutchison and Dr. Vanessa De Castro for helping with HRTEM observations and obtaining CBED patterns, respectively.

3.3. Determination of the Mechanical Properties

3.3.1. Indentation Studies

For evaluating the hardness (H_v) of the Al_2O_3 -based and ABS-based samples, Vickers indentations (AVK-C1/C2, Mitutoyo) were obtained on the polished surfaces with

indentation loads (P) of 5 kg and 2 kg respectively and for loading times of 15s. Additionally, for the ABS-based samples, hardness and Young's modulus (E), were also estimated from measurements made with a depth sensing Berkovich nanoindenter (XP, MTS NanoInstruments, Oak Ridge, TN, U. S. A), using the methodology proposed by Oliver and Pharr [12-14].

The indentation fracture toughness (K_{Ic}) was evaluated for the Al_2O_3 -based materials by crack length measurement of the radial crack patterns formed around Vickers indents and adopting the following formulation proposed for radial-median crack systems, by Anstis et al. [15];

$$K_{Ic} = 0.016 (E/H_v)^{1/2} (P/c)^{3/2} \quad (3.1)$$

where E is the elastic modulus, estimated using 'rule of mixture calculations'. It is to be noted here that, since the c/a (where, c = half crack length of a radial crack and a = half diagonal length of an indent) ratios, calculated from the SEM images of the indentation induced cracking, are ≥ 3 , the developed crack system can be classified as radial-median (half-penny cracks) [15-19]. The reported values are the average of data obtained from at least five indentation tests.

3.3.2. Bend Tests

Flexural strengths were measured using rectangular cross-section beams tested in four-point bending. With regard to fracture toughness measurement, considering the unreliability of earlier results obtained for various ceramics using the indentation-crack length measurements [20,21] and following the demonstration by Wang et al. [22] that this technique can be particularly misleading for CNT reinforced ceramic composites, we have used the more reliable Single Edge V-Notch Beam (SEVNB)

technique to measure the fracture toughness of the ABS as well as Al_2O_3 -based materials. For the flexural strength and fracture toughness measurements, as-cut beams were polished on both narrow long faces and one broad long face using 25, 6, 3 and 1 μm diamond slurries. The final specimen dimensions were 13 mm $\times$ 2.5 mm (W) $\times$ 2 mm (t). For SEVNB, the ratios between the notch depths and specimen thickness were between 0.2-0.3. The notches were sharpened by razor blade so that the tip radii of the notches were less than $\sim 10 \mu\text{m}$. The flexural strengths and fracture toughness were measured in the four-point bending configuration, using a crosshead loading rate of 5 N/min and inner and outer spans of 5.8 and 10 mm, respectively. The tests were performed on a universal testing machine (Dension-Mayes, U.K.). The set up for the bend tests is schematically presented in Fig. 3.4.

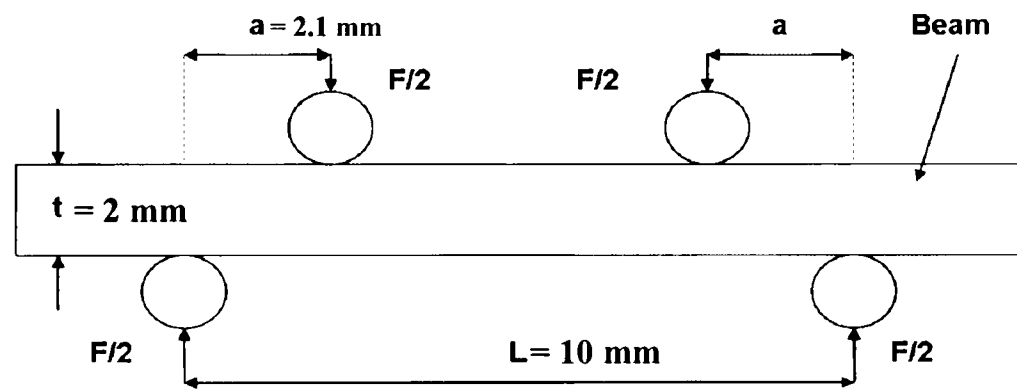


Fig. 3.4. Schematic representation of the 4-point bending set up, used for measuring the flexural strengths and fracture toughnesses.

The flexural strength (σ_f) was estimated using the following relation;

$$\sigma_f = \frac{3 \times F_{\max} \times a}{W \times t^2} \quad (3.2)$$

where $F_{\max}$ is the maximum load, W is the beam width, t is the specimen thickness and a is as defined in Fig. 3.3.

For estimating the fracture toughness, the following relation was used [23];

$$K_{1c} = \frac{P_f(L_o - L_i)}{BW^{3/2}} \frac{3\alpha^{1/2}}{2(1-\alpha)^{3/2}} f(\alpha) \quad (3.3)$$

$$f(\alpha) = 1.9887 - 1.326\alpha - \frac{\alpha(1-\alpha)(3.49 - 0.68\alpha + 1.35\alpha^2)}{(1+\alpha)^2} \quad (3.4)$$

where P_f , L_o , L_i , B , W are experimentally measured fracture (maximum) load, outer span, inner span, specimen width, and specimen thickness, respectively. The pre crack size (notch depth) enters the equation through α , where $\alpha = a/W$. The reported values are the averages of at least 5 independent measurements.

3.4. Abrasive Wear Tests for the Al_2O_3 -based Particulate Nanocomposites

A standard abrasive wear test, based on the use of a load-controlled grinding/polishing machine (MOTOPOL 2000, Buehler, UK) under standard conditions, was used to investigate the wear resistance of monolithic Al_2O_3 , as sintered Fe containing Al_2O_3 and samples aged under optimum aging conditions. All the samples were in the form of pellets of 10 mm diameter and 3 mm thickness. The samples were attached using adhesive (super glue) to resin cylinders (i.e. dummy metallographic specimens) in the standard carousel for metallographic preparation. The grinding was conducted using a 305 mm diameter resin-bonded alumina plate (Kemet, UK) with an oil-based suspension of 45 μm diamond abrasive. The specimens were ground for 4 minutes with the grinding plate and specimen holder rotating in opposite directions. The rotation speed of the grinding plate was 350 rpm and a force of 22.2 N per sample was applied. A standard charge of diamond spray

was applied every 20 seconds. A schematic representation of the set up used for the wear tests is presented in Fig. 3.5. This set up has been extensively used in our group for investigating the abrasive wear behaviour of Al_2O_3 - SiC nanocomposites [11,24].

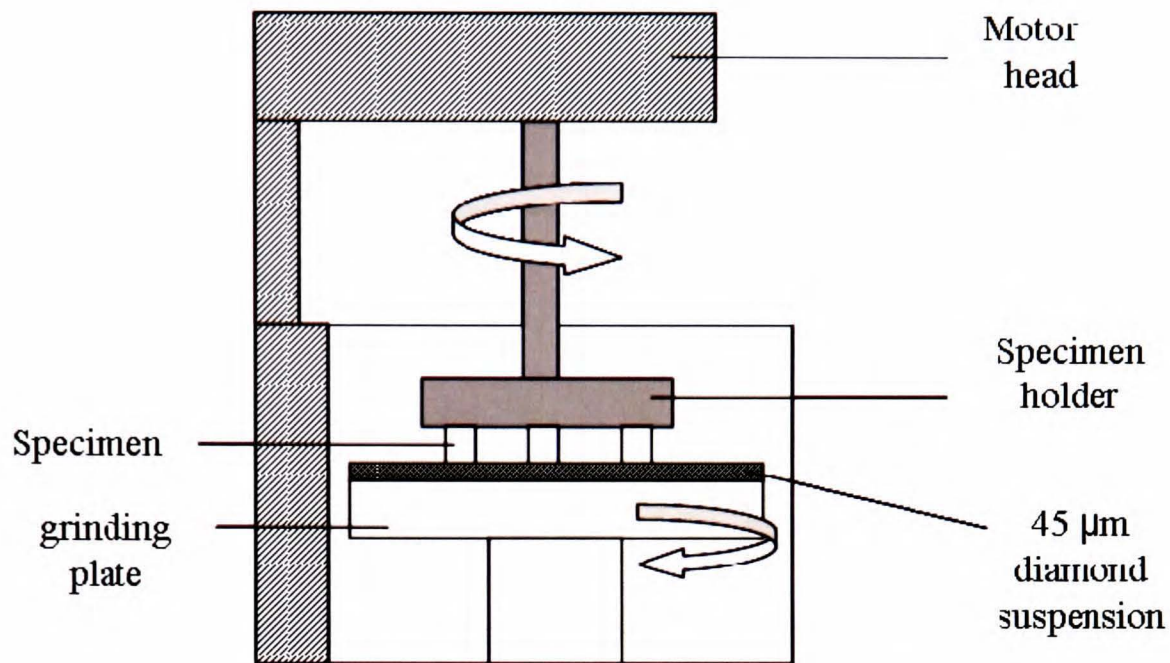


Fig. 3.5. Schematic representation of the load-controlled grinding/polishing machine used for the abrasive wear tests.

The mass loss during the test (Δm) was determined by weighing the specimens before and after each test. The wear rate (v) was defined as;

$$v = \Delta m / (\rho a t) \quad (3.5)$$

where A is the contact area, t is the testing time and ρ is the density of the material.

The wear rate can be viewed as the velocity with which the surface recedes, or equivalently, the volume of material removed per unit contact area per unit time.

Following initial bedding in, at least four of these standard tests were performed for each material. The worn surfaces of the different samples were observed in SEM (JEOL 6500F). Prior to SEM observations, the worn samples were cleaned in ultrasonic bath using ethanol. Similar to the estimations concerning the area fraction and sizes of the second phase particles from BSE-SEM images (section 3.2), for some

of the worn specimens, the area fractions of pullout caused by brittle fracture were measured by linear intercepts with lines in a grid on SEM micrographs. The pullout sizes were measured as the mean linear intercept multiplied by a factor of 1.27 to obtain an equivalent circular diameter [11]. Some of the worn surfaces were also subjected to XRD investigations.

3.5. Indentation Polish Tests for the Al₂O₃-based Particulate Nanocomposites

Vickers Indentations were obtained using 10 kg load on the polished surfaces of monolithic alumina, A10F solid solution and the samples aged for optimum durations at 1450°C. The indented surfaces were subsequently polished with 1 µm diamond paste on a soft cloth using the automated grinding polishing machine (MOTOPOL 2000, Buehler, UK) until only the lower tip of the original indentation remained. In order to observe the presence of possible grain pull outs or any other damages that might have occurred beneath the indentations during polishing, the as polished surfaces near the residual indents were observed in SEM (JEOL 6500F).

3.6. Electrical and Thermal Properties of ABS - MWCNT Nanocomposites

3.6.1. Electrical Resistivity Measurements

A four-point probe device (Resistivity Test Rig, Model A A, M. Fell Ltd., UK) was used to measure the electrical resistivity of the materials. The rig consists of four tungsten metal tips equally spaced at 1 mm and fixed to a mechanical stage with springs. Impedance current was applied to go through the outer two probe tips, and a

voltage across the inner two probe tips was measured by a voltmeter. A schematic representation of the test set up is presented in Fig. 3.6.

For the bulk samples of monolithic ABS and ABS - MWCNT nanocomposites, the electrical resistivities have been calculated according to the following equation [25];

$$\rho = 2 \pi s \left(\frac{V}{I} \right) \quad (3.6)$$

where s ($= 1 \text{ mm}$) is the probe spacing, I is the current applied at the outer two probe tips, and V is the voltage generated between the inner two probe tips as measured using a voltmeter.

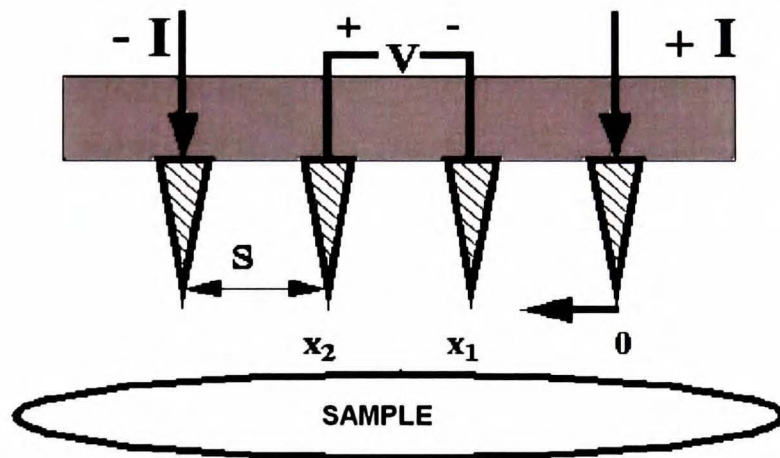


Figure 3.6. Schematic representation of the four-point probe set up for measurement of electrical resistivity.

3.6.2. Thermal Diffusivity Measurements

The room temperature thermal diffusivities of the monolithic and nanotube reinforced glass-ceramics were measured using a laser flash technique. The bulk samples were cut into disc shaped specimens of 10 mm diameter and 1.5 mm thickness. In the apparatus the heat pulse was supplied by a 100 J Nd-glass laser with a wavelength of

1.067 μm [26]. The disc-shaped specimens were mounted in a graphite holder located inside a graphite susceptor. The susceptor was placed inside an induction coil at room temperature under air. Radiation from the rear face of the specimen was collected via a lens and a mirror system and focused on to an indium antimonide infrared detector. The biased output from the detector was amplified and connected to a PC via digital converter where the thermal diffusivity values were recorded. A schematic of this laser flash equipment is presented in Fig. 3.7 [27]. NIST Stainless Steel:1461 and Poco Graphite AXM 5Q1 having thermal diffusivities of 0.037 and 0.74 cm^2/s , respectively, were used for calibrating the instrument. The author would like to thank Mr. Andrew Wallwork, University of Manchester, for performing the Thermal Diffusivity measurements.

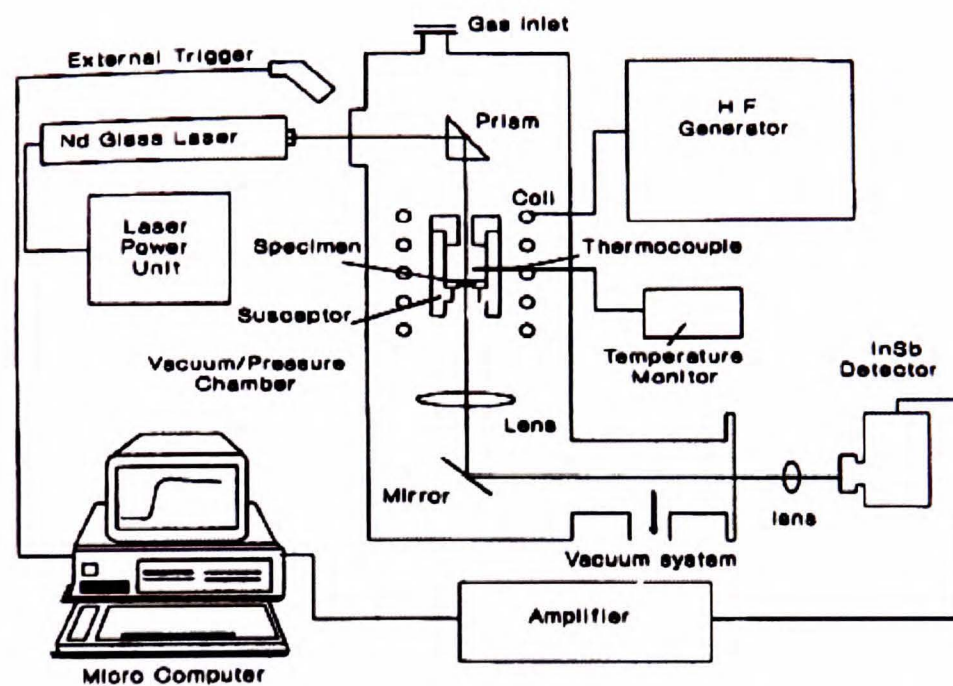


Figure 3.7. Schematic representation of the laser flash equipment used for measuring the thermal diffusivities [27].

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Chapter 4

PROCESSING, MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Al_2O_3 -BASED PARTICULATE NANOCOMPOSITES

The possibility of development of nano-particulate reinforced bulk ceramic nanocomposites via a novel solid state precipitation route has been explored. The microstructural development obtained during heat treatment at different temperatures and for different durations has been discussed in the following sections. The mechanical properties of the nanocomposites developed under the optimum processing conditions are also reported and discussed in relation to the microstructural development.

4.1. Results

4.1.1. Phase Evolution and Microstructural Development

4.1.1.1. Phase Evolution

The phase evolutions during the different processing steps, which include solution treatment (sintering) and aging at different temperatures (1250°C - 1550°C) in reducing ($N_2 + H_2$) atmosphere, have been extensively studied using X-ray diffraction. A few selected XRD patterns, recorded with as sintered pure Al_2O_3 , calcined Fe-containing Al_2O_3 (A10F) pellets, solution treated A10F and aged (1450°C; 0 - 50 hrs; $N_2 + 4\% H_2$ atmosphere) A10F are presented in Fig. 4.1. It must be mentioned here that the XRD patterns, as presented in Fig. 4.1, have been recorded from corresponding ground and polished surfaces, which make them representative of the sample cores.

Pattern 2 of Fig. 4.1 reveals that after calcination at 750°C for 1 h, the $Fe(NO_3)_3 \cdot 9H_2O$ precursor has decomposed to $\alpha-Fe_2O_3$, which is present as a secondary phase along with $\alpha-Al_2O_3$ in the as calcined pellets. On the other hand, in the XRD pattern corresponding to the as sintered A10F (pattern 3) the presence of peaks corresponding

to only α - Al_2O_3 can be detected (compare with pattern 1). The absence of any other peaks corresponding to any possible secondary phase(s), in particular that of α - Fe_2O_3 , indicates that Fe_2O_3 (~ 10 wt.%) gets completely dissolved in the Al_2O_3 matrix during holding at the sintering temperature of 1450°C . The formation of such single phase Al_2O_3 - 10 wt.% Fe_2O_3 solid solution, during sintering at 1450°C for 5 h in air (solution treatment), is in accordance with the published Al_2O_3 - Fe_2O_3 phase diagram [1]. It can be further observed from the magnified view of the (104) peak of α - Al_2O_3 (Fig. 4.1b) that there is a notable shift in the peak position towards the lower angle (2θ) side after solution treatment of A10F (compare patterns 1 and 3). Since the ionic radius of Fe^{3+} (0.065 nm) is comparatively larger than that of Al^{3+} (0.054 nm), dissolution of Fe^{3+} in the Al_2O_3 matrix via substituting for the Al^{3+} in the cationic sublattice [2] leads to the expansion of the lattice and hence results in the corresponding shifts in peak positions towards lower Bragg angles.

The most significant result, as obtained from the XRD investigations, has been the appearance of peaks corresponding to FeAl_2O_4 (iron aluminate spinel) on aging of solution treated A10F for different durations (0 - 50 h) at temperatures varying between 1250°C and 1550°C in reducing atmosphere ($\text{N}_2 + \text{H}_2$ gas mixture). Patterns corresponding to the samples aged for 0 h (pattern 4), 20 h (pattern 5) and extended duration of 50 h (pattern 6) at 1450°C are presented in Fig. 4.1a. Additionally, peaks corresponding to α - Al_2O_3 get shifted back towards higher Bragg angles on reduction aging of the solid solutions (compare patterns 1 and 3 in Fig. 4.1b). This is consistent with the decrease in lattice parameter due to diminution of the Fe present in solid solution. Hence, the XRD results reveal that aging of the supersaturated solid solution of A10F under reducing conditions ($\text{N}_2 + \text{H}_2$ gas mixture) results in the precipitation of FeAl_2O_4 as the equilibrium secondary phase.

The amount of secondary phase (FeAl_2O_4) getting precipitated in the Al_2O_3 matrix, which is in turn related to the fraction of the dissolved Fe^{3+} getting released from solid solution, has been found to vary considerably with the aging temperature and time. Insight into such effects of the aging temperature and time on the progress of the precipitation reaction can be obtained by estimating the decrease in the interplanar spacing of the matrix (Al_2O_3) with respect to the solution treated A10F caused by the diminution of Fe^{3+} from the solid solution. Such change in interplanar spacing has been estimated from the shifts of the (113) and (226) Al_2O_3 peak positions in the XRD patterns obtained with samples aged for different temperature - time schedules. It can be seen from Fig. 4.2a that the extrapolation procedure [3] used to determine the accurate values of the interplanar spacings results in convergence of the three lines joining the values obtained with the (113) and (226) peaks for the same sample, as $(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$ approaches zero, which corresponds to the true value of d_{113} .

Plot showing the variations of the changes in Al_2O_3 interplanar spacing with aging duration at the different aging temperatures (1250°C, 1350°C, 1450°C and 1550°C) is presented in Fig. 4.2b. It can be observed that interplanar spacing decreases with time at all three aging temperatures. However, as compared to the lower temperatures (1250°C and 1350°C), the activity is significantly higher at the higher temperatures (1450°C and 1550°C). Furthermore, the plots indicate that the precipitation reaction seems to reach equilibrium after ~ 15 h at 1450°C and only ~ 10 h at 1550°C, with no further diminution of dissolved Fe^{3+} on further increase in aging time. On the other hand, at the lower temperatures the interplanar spacing continued to decrease with increase in duration up to 50 h, with no indication of the precipitation reaction reaching equilibrium even after aging for such an extended duration.

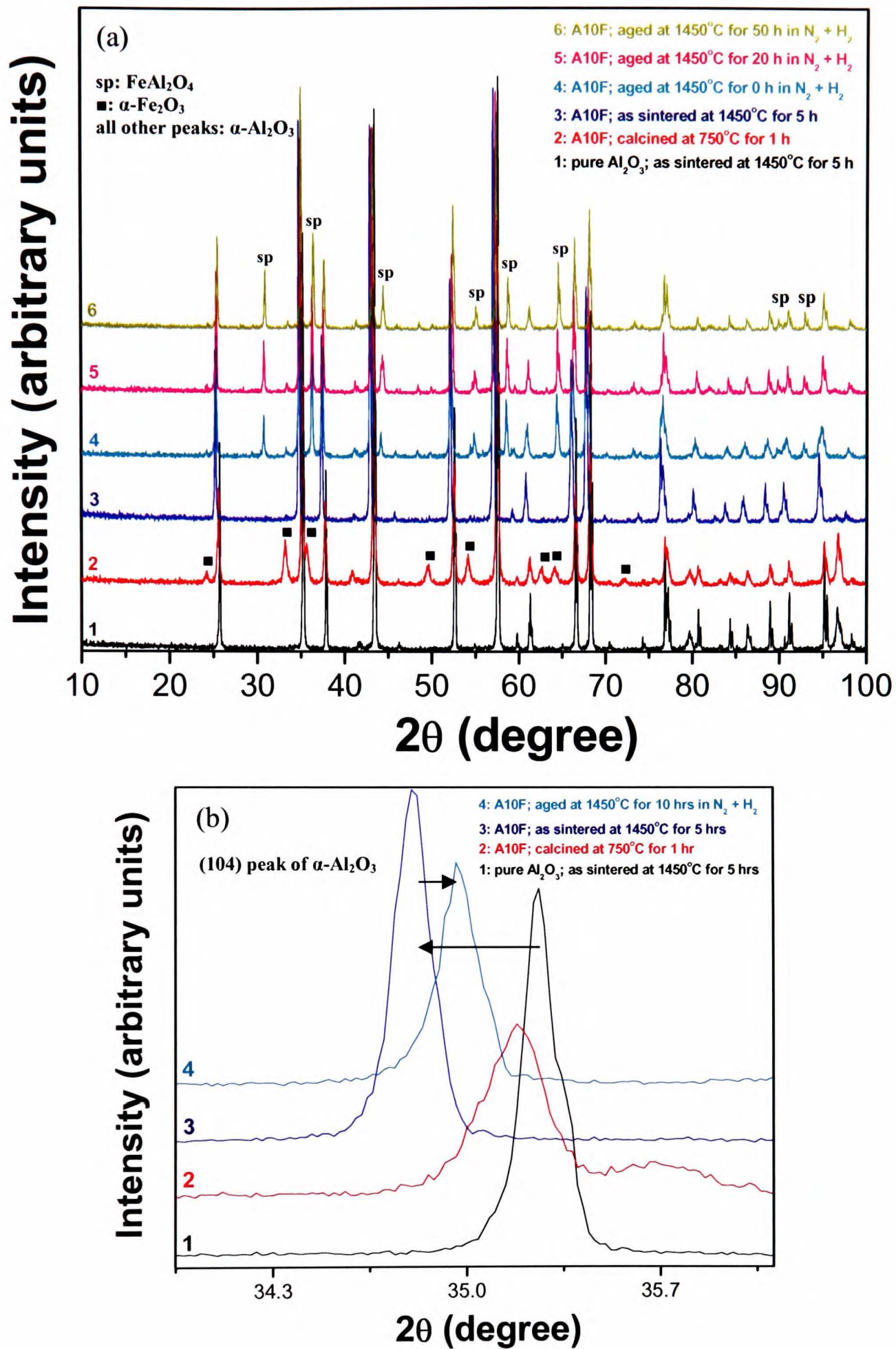


Fig. 4.1. (a) XRD patterns obtained from calcined A10F pellets and polished surfaces of as sintered pure Al_2O_3 and A10F as solution treated and after subsequent aging at 1450°C for 0, 20 and 50 hrs in reducing atmosphere ($\text{N}_2 + 4\% \text{H}_2$ gas mixture). Note the appearance of spinel phase on aging of the supersaturated A10F solid solution; (b) Magnified view of the {104} peak of $\alpha\text{-Al}_2\text{O}_3$ showing peak shifts after solution treatment and aging.

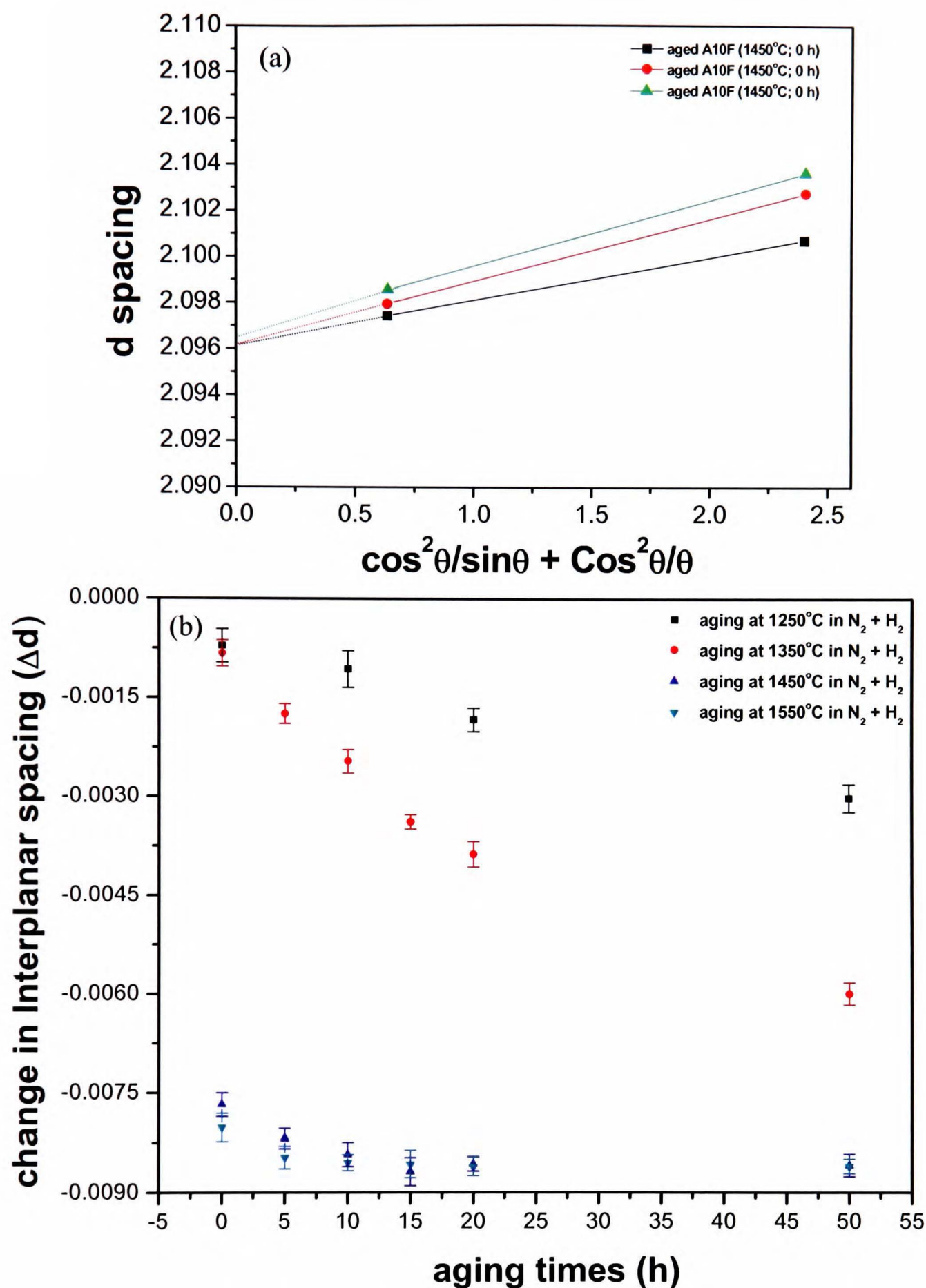


Fig. 4.2. (a) Plot of d-spacing against the extrapolation function, $(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$, used to determine the accurate values of the interplanar spacings (d_{113}). Note that the three lines corresponding to the three measurements done with three different scans on the same sample (A10F; aged at 1450°C for 0 h) converge as $(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$ approaches 0. (b) Change in $\{113\}$ interplanar spacing of matrix with aging time at the different aging temperatures (1250°C - 1550°C), as estimated from the shifts in the $\alpha\text{-Al}_2\text{O}_3$ peak positions in the as aged (A10F) samples with respect to the peak positions of the as sintered A10F solid solution.

4.1.1.2. Microstructural Development

4.1.1.2.1. As Sintered Microstructures

Fig. 4.3 presents representative back scattered scanning electron micrographs (BSE) of polished and thermally etched surfaces of as sintered monolithic Al_2O_3 , A10F as well as Y_2O_3 doped (250 ppm) A10FY. The absence of significant residual porosity, as observed from the micrographs of all the sintered samples, was confirmed by the density measurements which showed that all the samples were densified to $> 98\%$ of their theoretical density. It is evident from Fig. 4.3 that the presence of dissolved Fe considerably alters the size and morphologies of the Al_2O_3 grains. For pure Al_2O_3 the grains are fairly equiaxed in shape, without any observable abnormal or anisotropic grain growth (Fig. 4.3a), with the grain sizes varying between 2 - 4 μm . By contrast, the Fe-containing samples show microstructures characterised by the presence of a few large elongated grains in a matrix of finer equiaxed grains. The equiaxed grains possess sizes ranging between 1 - 3 μm , while some of the elongated grains have lengths varying between 5 - 8 μm and widths between 2 - 3 μm (Fig. 4.3b,c).

Probably the most important observation is that no evidence of any secondary phase can be detected on the BSE images of the as sintered (solution treated) Fe_2O_3 containing Al_2O_3 (Fig. 4.3b,c). Furthermore, the absence of significant amounts of secondary phase either along the matrix grain boundaries or within the matrix grains was also confirmed by TEM investigation (Fig. 4.3d). In accordance with the XRD results these observations further confirm that the sintering (solution treatment) step results in complete dissolution of 10 wt.% Fe_2O_3 in Al_2O_3 . Such results are in agreement with published pseudo binary phase diagrams of the Al_2O_3 - Fe_2O_3 system [1].

The distribution of the various elements (Al, Fe, O) present in the microstructure of as sintered A10F has been revealed by X-ray elemental mapping (Fig. 4.4a). The important observation is that Fe is distributed uniformly throughout the microstructure. Furthermore, a line scan across a grain boundary reveals that there is no apparent segregation of Fe in the grain boundary region (Fig. 4.4b). Within the limits of X-ray mapping performed in FEG-SEM, no preferential segregation of dissolved Fe along the matrix grain boundaries can be observed in the as sintered microstructure, which is in agreement with an earlier report by Tartaj and Messing [4].

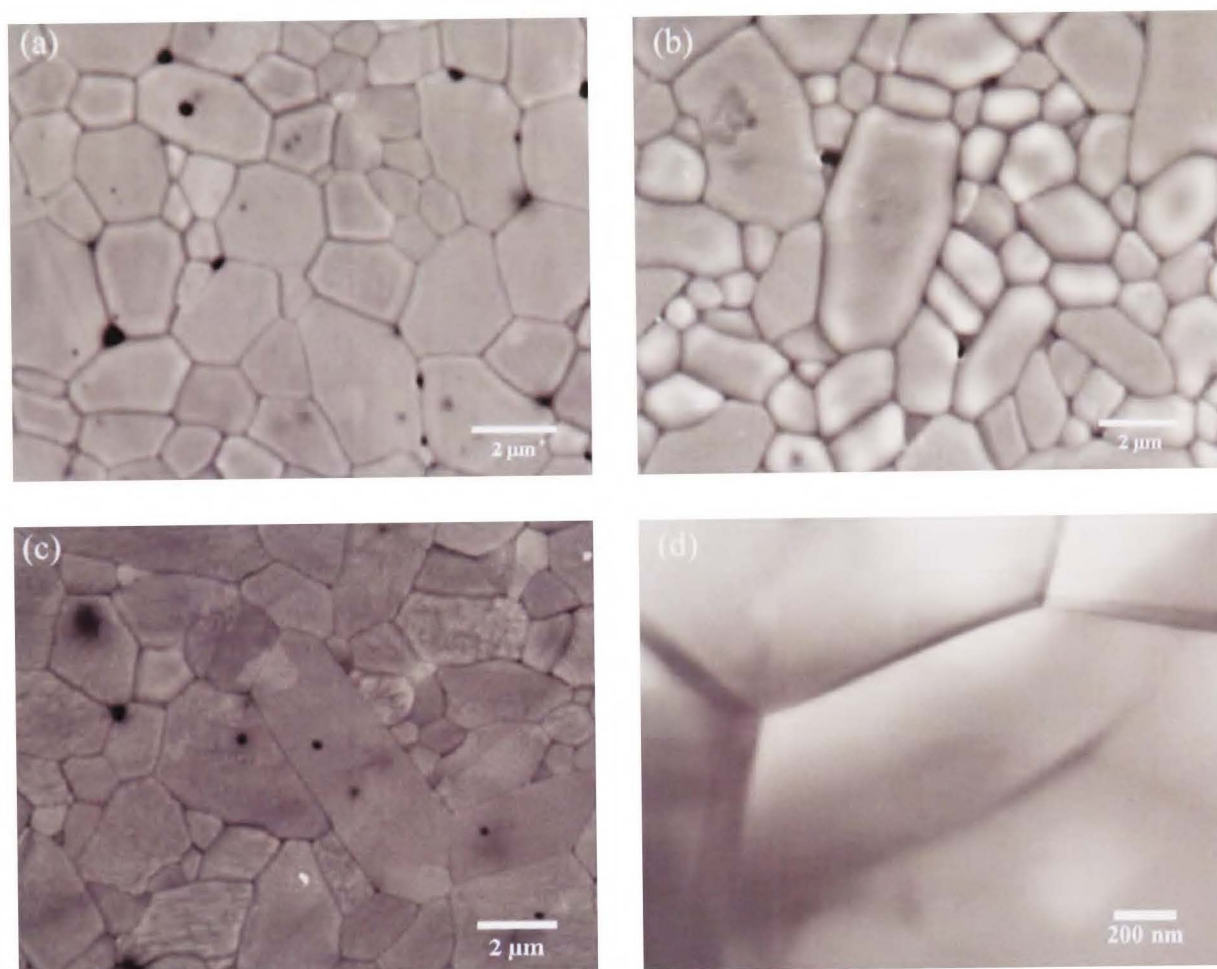


Fig. 4.3. Back scattered scanning electron micrographs (BSE-SEM) obtained from polished and thermally etched surfaces of as sintered (a) pure Al_2O_3 ; (b) A10F and (c) A10FY (doped with 250 ppm of Y_2O_3). TEM image corresponding to as sintered (solution treated) A10F, confirming the absence of any secondary phase along the matrix grain boundaries or within the grains.

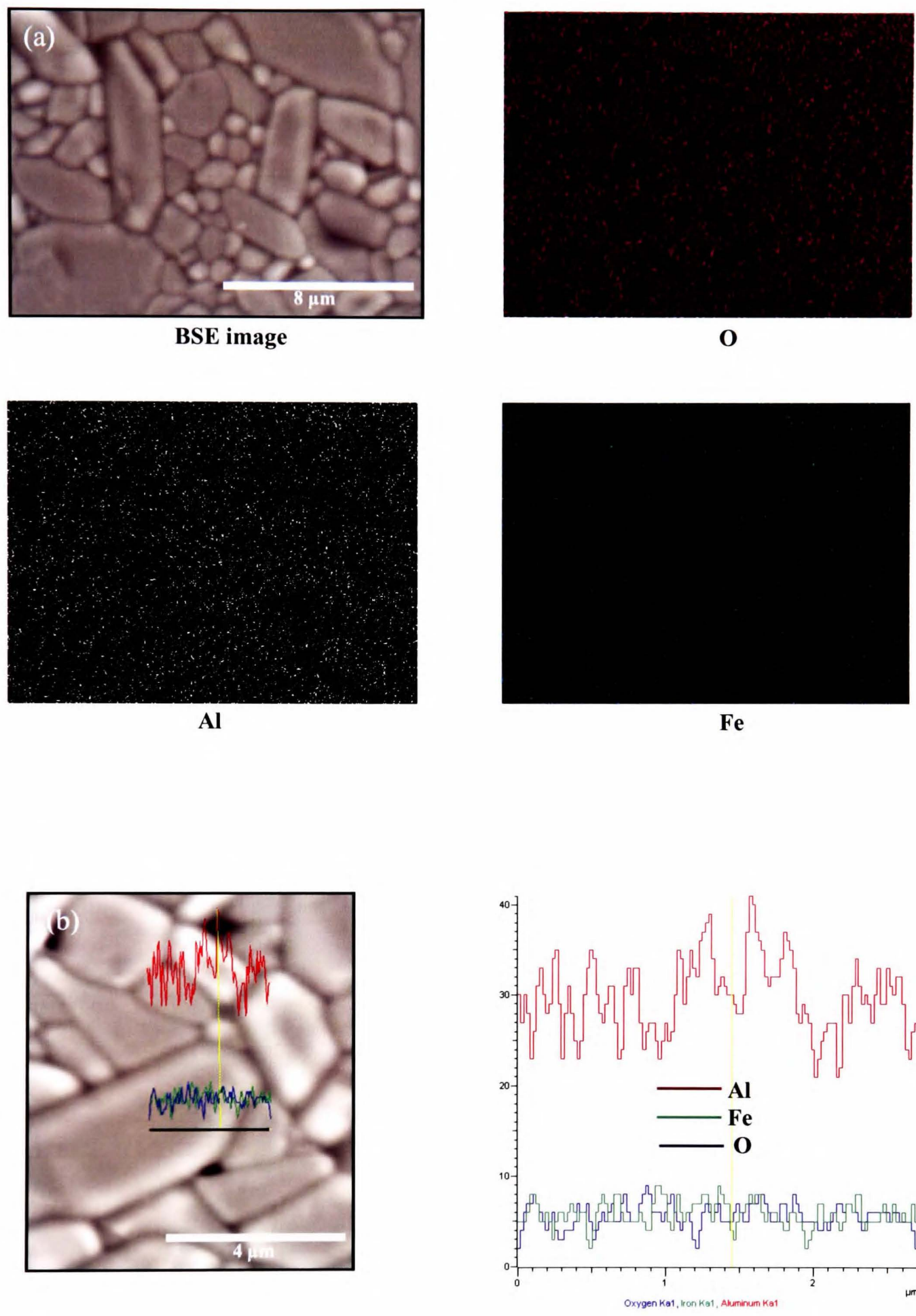


Fig. 4.4. (a) X-ray elemental mapping, showing the uniform distribution of the various elements (Al, O, Fe) present on the polished thermally etched surface of as sintered A10F; (b) Line scan obtained across a grain boundary in as sintered A10F.

4.1.1.2.2. Bulk Microstructural Development on Aging

Back scattered SEM (BSE-SEM) images obtained from near the cores of the samples, aged at the various temperatures for different durations in the reducing atmosphere, are shown in Figs. 4.5 - 4.7. The presence and average sizes of the inter- and intra-granular second phase particles corresponding to the different aging schedules, as estimated from the BSE-SEM images, are also reported in Table 4.1. The presence of a secondary phase (brighter contrast) is clearly revealed in the BSE-SEM images corresponding to the ground and polished surfaces of the samples aged for the maximum duration of 50 h at the lower temperatures of 1250°C and 1350°C (Fig. 4.5a,b). However this secondary phase is present only as coarse, micro-scale particles mainly along the boundaries and at the triple point corners of the matrix grains. The precipitation of second phase particles within the matrix grains seems to be severely hindered at these lower temperatures, even on holding for an extended period of time (50 h).

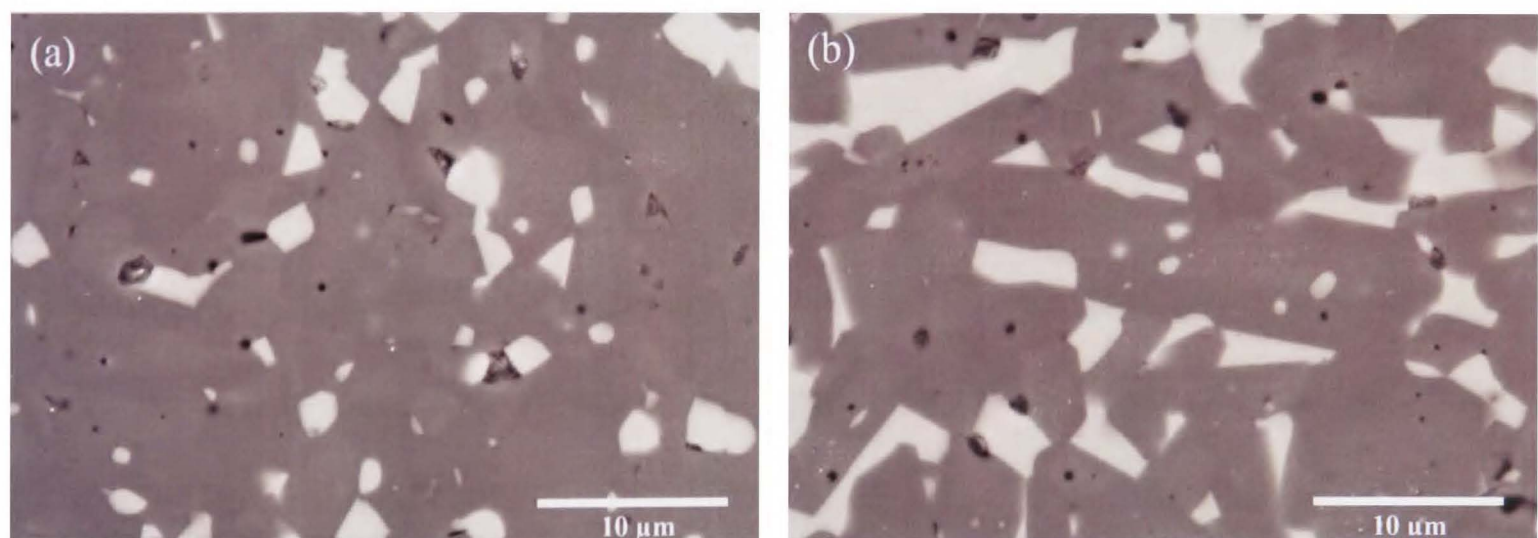


Fig. 4.5. BSE-SEM images obtained from ground and polished surfaces (sample core) of A10F, aged for extended duration of 50 h in reducing atmosphere ($N_2 + 4\% H_2$) at the lower aging temperatures of (a) 1250°C and (b) 1350°C.

The bulk microstructures after reduction aging at 1450°C for different times are presented in Fig. 4.6. Again, only micro-scale grain boundary particles appear during the initial stages (0 - 5 h) of aging (see Fig. 4.6a). However, on continued aging for durations of 10 hrs or more at 1450°C, extremely fine ‘nano-sized’ second phase particles (~ 70 nm) precipitated within the matrix grains, along with the continuing presence of the coarser intergranular particles (Fig. 4.6b). On further aging (up to 20 h) modest coarsening of both the inter- and intra-granular particles (Fig. 4.6c) occurred. On aging for the extended duration of 50 hrs at 1450°C significant microstructural coarsening occurred, with the intragranular particles growing to submicron size (~ 0.3 µm) along with the formation of a nearly interconnected network of intergranular spinel phase (Fig. 4.6d). EDS spectra confirm the presence of more Fe in the second phase particles than in the matrix (Fig. 4.6). It must be noted that the intragranular particles retained a nano or sub micron size for all the aging schedules studied (see Table 4.1).

Excessive coarsening of the intergranular FeAl₂O₄ particles, as observed for the samples aged for 50 h at 1450°C (Fig. 4.6d), also occurred during aging at the highest investigated aging temperature of 1550°C even for much shorter durations (~ 10 h) (Table 4.1 and Fig. 4.7). Precipitate free zones, which usually form due to the depletion from near the grain boundary regions of the solute atoms which join the heterogeneously nucleated intergranular precipitate particles, can also be observed near the grain boundary particles in the BSE micrographs of the as aged samples (Fig. 4.6c,d and 4.7). Another interesting observation was that the composites containing such a coarse and inter-connected network of intergranular FeAl₂O₄ particles suffered considerable pull outs of these particles during metallographic polishing, which leads to a poorer surface finish for the ‘over-aged’ samples. This is in complete contrast to

the samples developed by aging for shorter duration (≤ 20 h) at 1450°C , which can be polished to a better surface finish and more easily than monolithic Al_2O_3 , as is the case for Al_2O_3 -SiC nanocomposites [5-7].

In the light of the literature reports claiming reduced diffusivities of species along the matrix grain boundaries due to the segregation of oversized Y^{3+} ions in the grain boundary regions of yttria doped polycrystalline Al_2O_3 [8-12], we have tried to explore whether Y_2O_3 doping (~ 250 ppm by weight) can suppress the formation of the relatively coarser intergranular particles. Fig. 4.8 presents BSE-SEM images obtained from polished surfaces of some of the yttria-doped samples (A10FY) subjected to reduction aging at 1450°C and 1550°C . It can be observed that though sub-micron sized intergranular second phase particles do appear in the nanocomposites developed via aging of the A10FY solid solutions, such particles are considerably smaller than those present in the nanocomposites developed via aging of the A10F solid solutions for the same duration at 1450°C . Furthermore, yttria doping minimizes the formation of an inter connected network of the FeAl_2O_4 particles formed on aging for the extended duration of 50 h at 1450°C . However, compared to aging at 1450°C , Y_2O_3 addition does not affect the microstructural development significantly during aging at 1550°C . Table 4.2 presents the sizes of the second phase particles as estimated from the BSE-SEM images of the nanocomposites developed during aging of A10FY solid solutions at 1450°C and 1550°C .

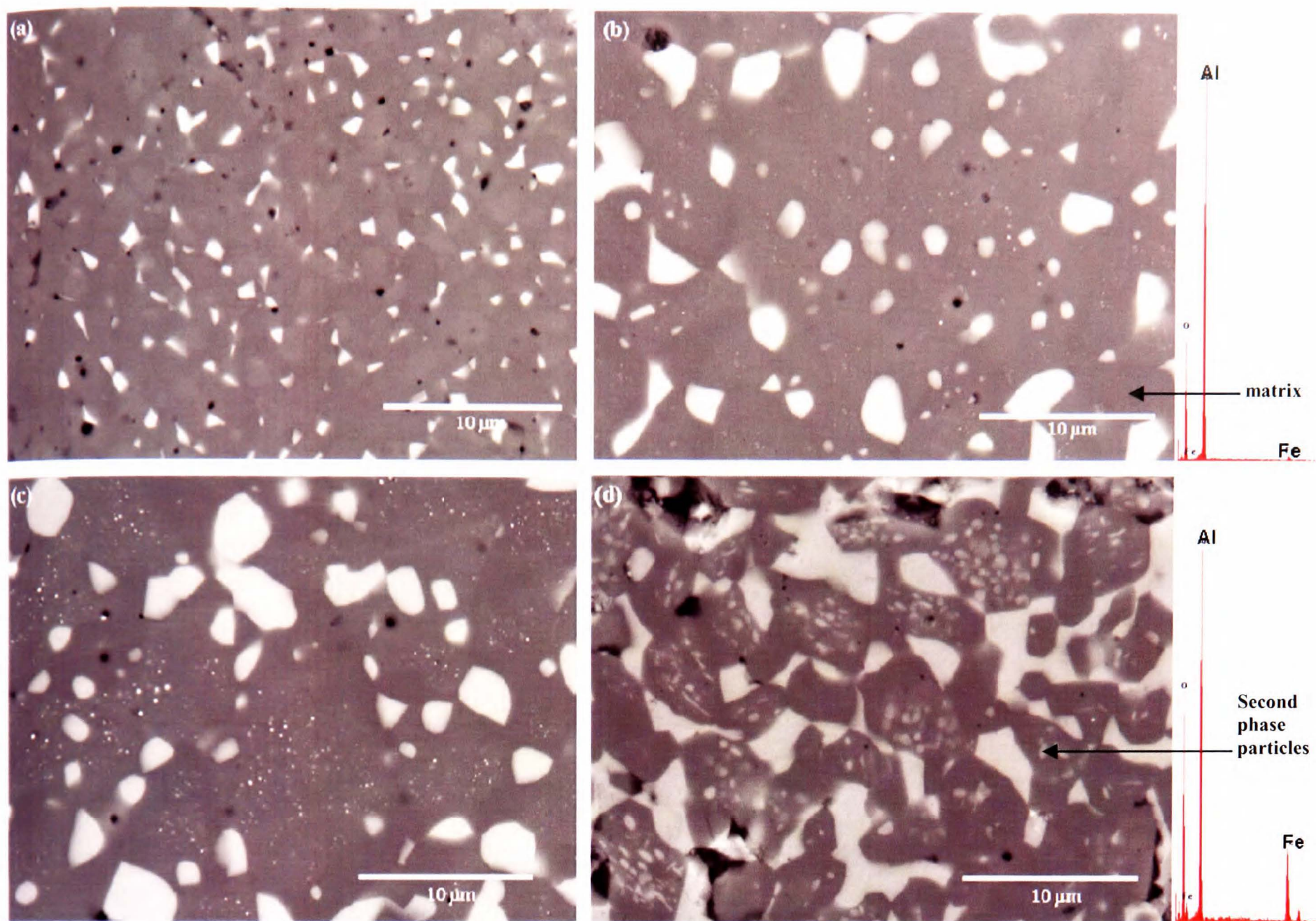


Fig. 4.6. BSE-SEM images obtained from the as ground and polished surfaces (sample core) of A10F, aged in reducing atmosphere ($N_2 + 4\% H_2$) at 1450°C for (a) 0 h; (b) 10 h; (c) 20 h; (d) 50 h. EDX spectra obtained from the matrix and the second phase particles are also presented.

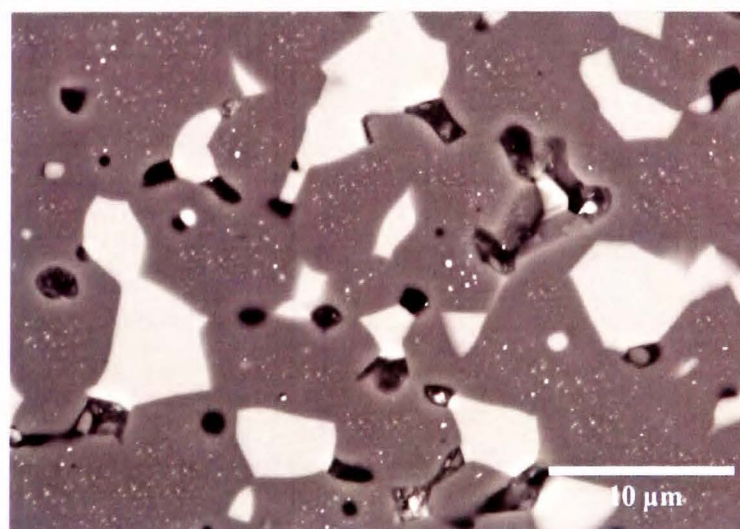


Fig. 4.7. BSE-SEM images obtained from the as ground and polished surfaces (sample core) of A10F, aged in reducing atmosphere ($N_2 + 4\% H_2$) at 1550°C for 10 h. Note the occurrence of significant microstructural coarsening, resulting in the presence of extremely coarse intergranular second phase particles.

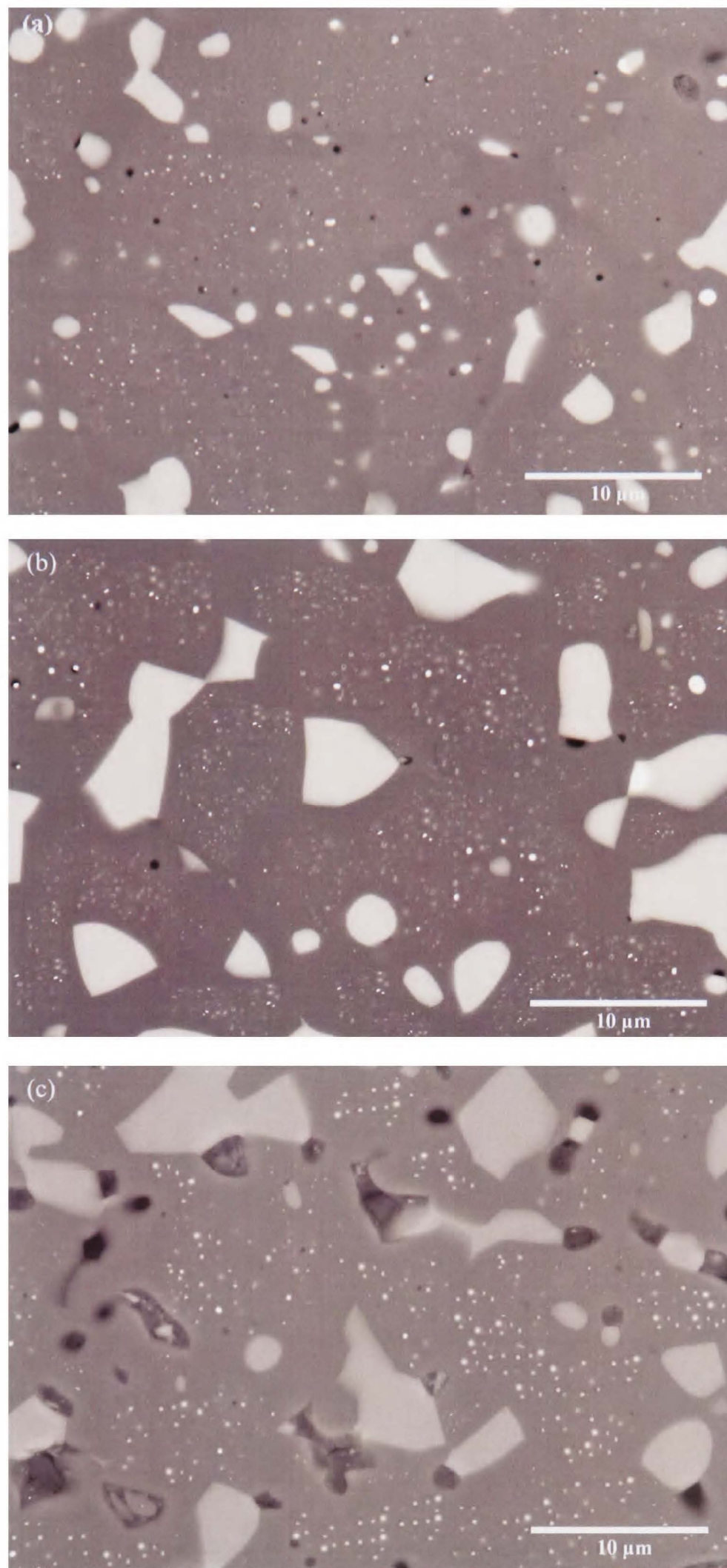


Fig. 4.8. Back scattered SEM micrographs obtained from the as ground and polished surfaces (sample core) of A10FY (Y_2O_3 doped ~ 250 ppm), aged in reducing atmosphere ($\text{N}_2 + 4\% \text{H}_2$) at (a) 1450°C for 20 h; (b) 1450°C for 50 h; (c) 1550°C for 10 h.

Table 4.1. Effect of aging temperatures (1250°C - 1450°C) and times (0 - 50 h) on the distribution and size of second phase particles (FeAl₂O₄) precipitated during aging of A10F solid solutions in reducing atmosphere (N₂ + 4% H₂).

Aging time (h)	Reduction aging temperature: 1250°C		Reduction aging temperature: 1350°C		Reduction aging temperature: 1450°C		Reduction aging temperature: 1550°C	
	Intergranular particles size (μm)	Intragranular particles size (nm)	Intergranular particles size (μm)	Intragranular particles size (nm)	Intergranular particles size (μm)	Intragranular particles size (nm)	Intergranular particles size (μm)	Intragranular particles size (nm)
0	0.8 ± 0.4	Not present	0.8 ± 0.7	Not present	1.1 ± 0.6	Not present	2.9 ± 0.6	Not present
5	-	Not present	1.1 ± 0.2	Not present	1.5 ± 0.8	Not present	5.4 ± 0.8	79 ± 17
10	1.2 ± 0.5	Not present	1.5 ± 0.4	Not present	1.7 ± 0.5	71 ± 27	Not measured due to excessive pull out	88 ± 19
15	-	Not present	1.8 ± 0.2	Not present	1.9 ± 0.5	104 ± 38	Not measured due to excessive pull out	119 ± 47
20	1.6 ± 0.3	Not present	2.2 ± 0.5	Not present	2.2 ± 0.3	127 ± 34	Not measured due to excessive pull out	153 ± 29
50	2.4 ± 0.7	Not present	5.1 ± 0.9	97 ± 21	Not measured due to network formation	321 ± 63	Not measured due to excessive pull out	521 ± 56

Table 4.2. Second phase particle sizes in the nanocomposites developed via reduction aging of the yttria doped Al₂O₃ - Fe₂O₃ (AFY) solid solutions.

Aging time (h)	Reduction aging temperature: 1450°C		Reduction aging temperature: 1550°C	
	Intergranular particles size (µm)	Intragranular particles size (nm)	Intergranular particles size (µm)	Intragranular particles size (nm)
0	0.6 ± 0.3	Not present	2.2 ± 0.4	27 ± 19
5	0.7 ± 0.9	29 ± 7	4.8 ± 0.3	74 ± 11
10	0.9 ± 0.6	68 ± 14	Not measured due to excessive pull out	102 ± 16
15	1.2 ± 0.7	92 ± 11	Not measured due to excessive pull out	114 ± 28
20	1.2 ± 0.3	108 ± 22	Not measured due to excessive pull out	159 ± 17
50	4.1 ± 0.8	204 ± 63	Not measured due to excessive pull out	497 ± 29

The percentage of the volume occupied by the secondary phase in the Al₂O₃ - FeAl₂O₄ ‘nanocomposites’, as determined via the point counting method from BSE-SEM images of the as aged A10F samples, is plotted as a function of the aging duration for the different aging temperatures in Fig. 4.9. It can be observed that, as compared to the higher temperatures of 1450°C and 1550°C, significantly lower amounts of secondary phase particles can be produced at the lower temperatures, reaching a maximum of only ~ 6 % at 1250°C and ~ 14 % at 1350°C even on aging for the extended duration of 50 h. By contrast, a volume percent as high as 19 - 20 % is achievable on aging at 1450°C for a period of 20 hrs or more. It must be mentioned here that the point count method may provide an underestimate of second phase content because some of the very tiny particles may not be detected during the

estimation and some of the coarser intergranular particles may be lost due to pull out during polishing (especially for the 1550°C aged composites).

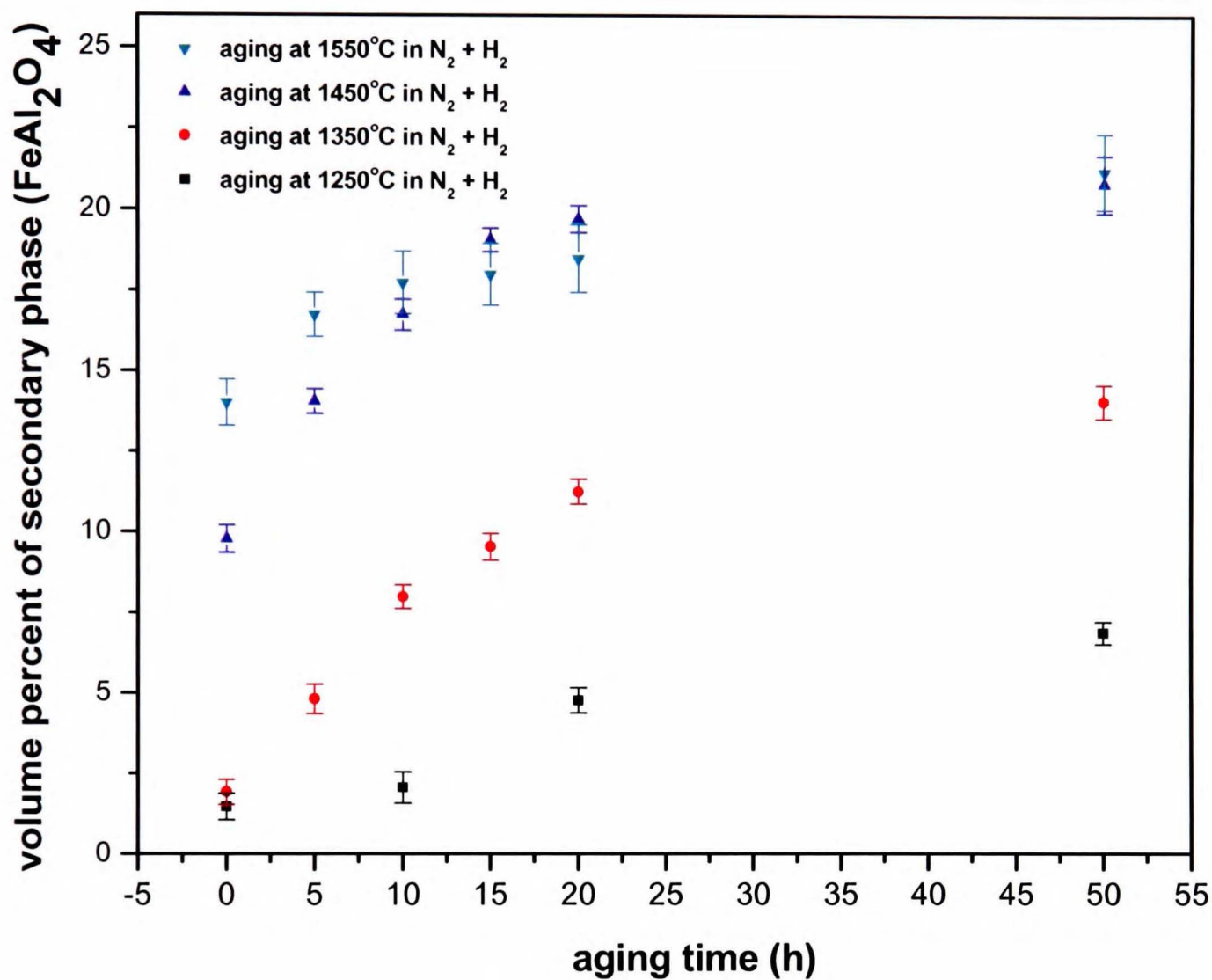


Fig. 4.9. Variation of volume percent of the secondary phase (FeAl₂O₄) formed as a function of aging time (0 - 50 h) at the different investigated aging temperatures (1250°C - 1550°C). The volume fractions have been estimated via point counting on back scattered SEM images.

Table 4.3 presents the ratios of the volume fractions occupied by the intra- and intergranular FeAl₂O₄ particles in the nanocomposites developed on aging of the A10F and A10FY solid solutions at 1450°C. It can be observed that the relative amounts of the intragranular nanosized particles, with respect to the coarser intergranular particles, increase with aging duration up to 20 h. On the contrary, there is no apparent increase in the ratios on continued aging up to 50 h. The important

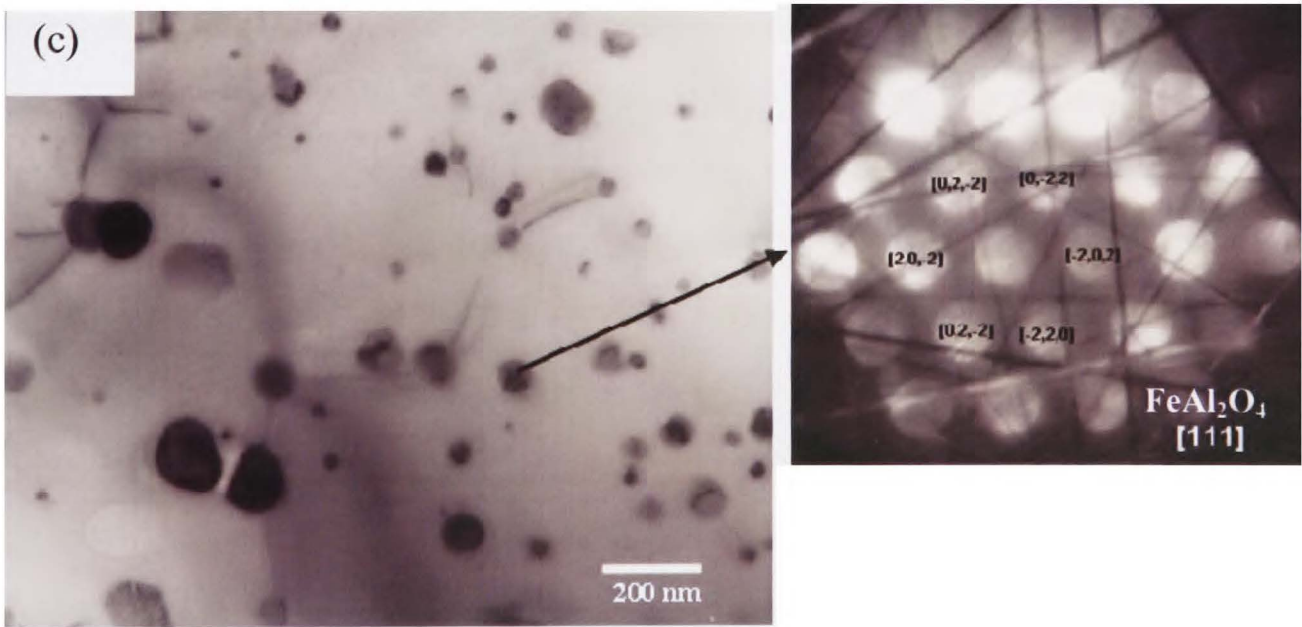
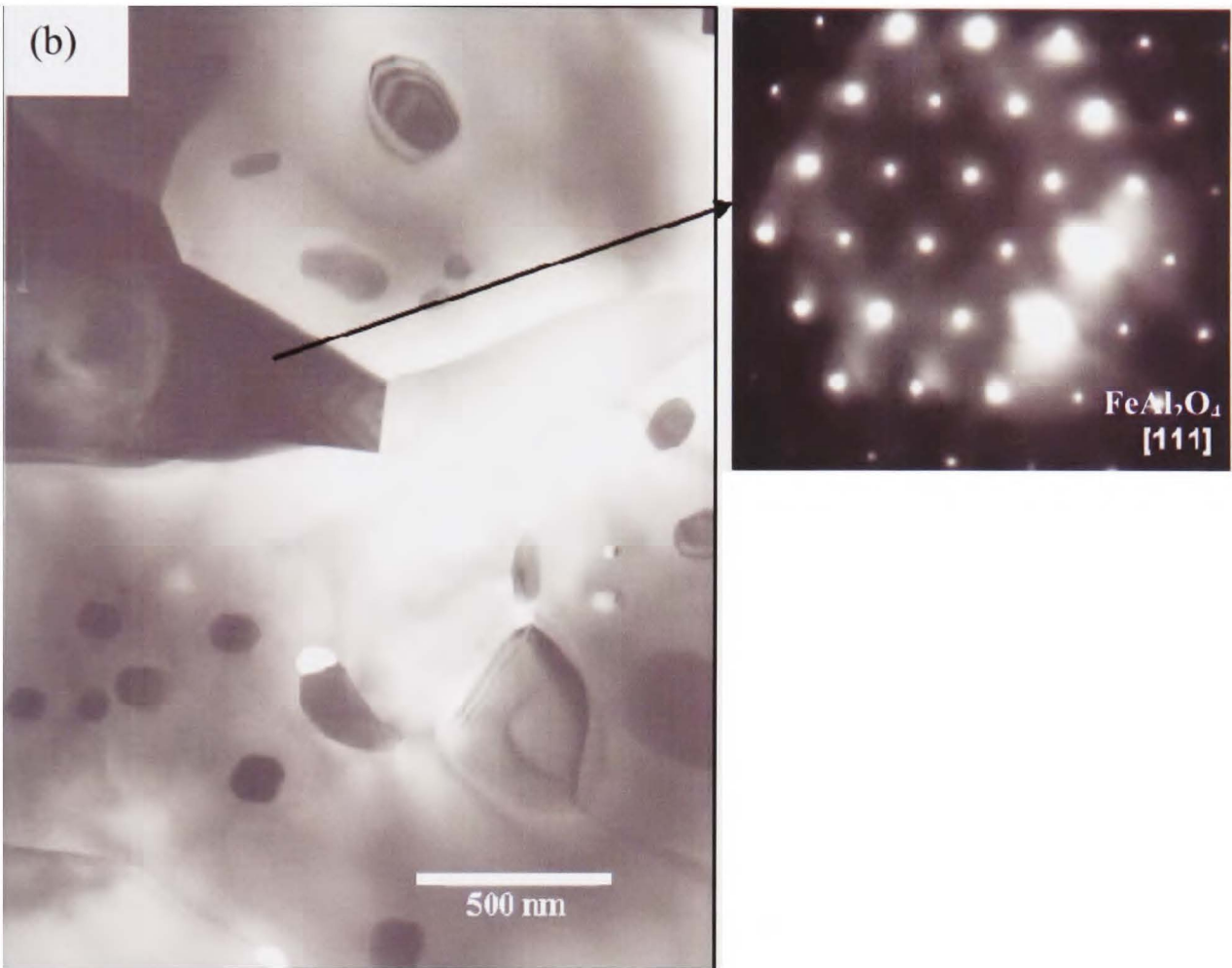
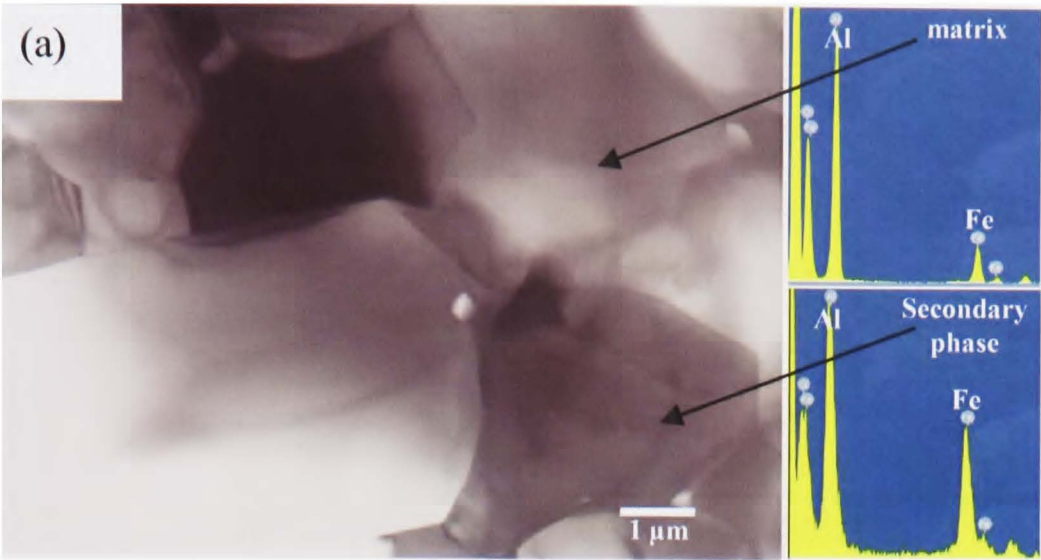
observation is that aging of the yttria containing solid solution (A10FY) results in the generation of higher relative amounts of intragranular particles, with respect to aging of A10F, at the corresponding aging durations.

Table 4.3. Ratios of volume fractions of intragranular particles to volume fraction of intergranular particles (R) obtained during reduction aging of the yttria-free (A10F) and Yttria-doped (A10FY) solid solutions at 1450°C.

Aging durations at 1450°C (h)	R obtained during aging of Yttria-free (A10F) solid solutions	R obtained during aging of Yttria-doped solid solutions (A10FY)
0	0	0
5	0	0.2 ± 0.07
10	0.3 ± 0.07	0.7 ± 0.02
15	0.5 ± 0.04	1.0 ± 0.08
20	0.9 ± 0.06	1.2 ± 0.14
50	0.9 ± 0.11	1.1 ± 0.09

The distribution of the second phase particles can be seen more clearly from the corresponding bright field transmission electron micrographs (TEM) (Fig. 4.10). In agreement with the SEM observations, the presence of only coarse intergranular second phase particles can be seen in the microstructures corresponding to the A10F samples aged at the lower temperature of 1350°C (Fig. 4.10a). By contrast, the

presence of nano-sized secondary phase particles within the matrix grains, along with coarser intergranular particles can be observed in the TEM images corresponding to the sample aged at 1450°C for optimum durations (Fig. 4.10b,c). It must be mentioned here that occasionally holes (1 - 2 μm in size) were observed along the boundaries or triple point corners of the matrix grains in the foils developed from the samples aged for 20 h (Fig. 4.10d). Such holes appear to have been formed due to the coarser intergranular particles falling out during the TEM sample preparation. For the as aged yttria doped samples (A10FY), the presence of comparatively finer micron sized intergranular particles, as compared to those in the A10F samples aged for the same duration at 1450°C, can be further confirmed TEM observations (Fig. 4.10e). Another interesting observation that can be made from the TEM images is the absence of strain contrast around the second phase particles for all the aging schedules studied. Elementary analysis via EDS shows that the second phase particles are Fe-rich relative to the bulk matrix (Fig. 4.10a). Furthermore, selected area diffraction patterns (SADP) obtained from the micron sized intergranular particles, as well as the convergent beam diffraction patterns (CBED) recorded from the nano-sized intra granular particles further reveals that the second phase particles present in the bulk microstructure of the as aged ‘nanocomposites’ are FeAl_2O_4 (Fig. 4.10b,c). Hence, TEM observations further confirm that such aging treatments can lead to the development of a ‘hybrid nano/micro composite’ microstructure of Al_2O_3 containing FeAl_2O_4 as second phase particles.



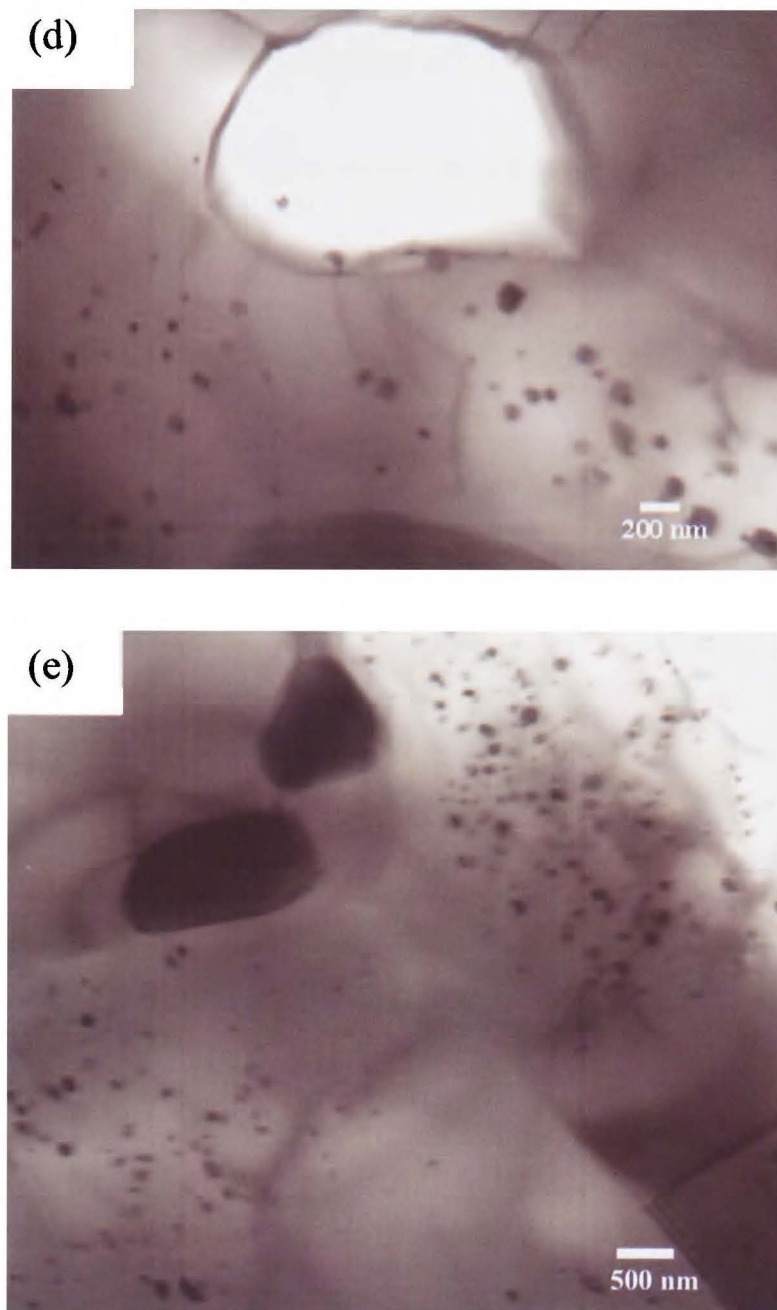


Fig. 4.10. Bright field TEM images corresponding to (a) as aged A10F (1350°C; 50 h; $N_2 + H_2$ atmosphere), revealing the presence of only coarse Fe-rich (see EDS spectra) secondary phase particles along the matrix grain boundaries; (b) as aged A10F (1450°C; 20 h; $N_2 + H_2$ atmosphere), revealing the presence of coarser second phase particles along the matrix grain boundaries, along with nano-sized particles within the matrix grains; (c) closer look at higher magnification within a matrix grain in as aged A10F (1450°C; 10 h; $N_2 + H_2$ atmosphere); (d) hole left along the matrix grain boundary possibly due to fall out of coarser inter granular particle during TEM sample preparation and (e) as aged A10FY (1450°C; 20 h; $N_2 + H_2$ atmosphere), revealing the presence of comparatively finer second phase particles along the matrix grain boundaries. Selected area diffraction patterns obtained from the coarser intergranular particles (b), as well as convergent beam diffraction patterns obtained from the nanosized intragranular particles (c), can be indexed with respect to $FeAl_2O_4$.

4.1.1.2.3. Effect of Reduction Aging on External Surfaces

The cross sections of the as aged samples were observed in SEM after cutting along a diameter of the pellets, followed by metallographic polishing. A cross section from a sample aged at 1450°C for 20 h in $N_2 + H_2$ is presented in Fig. 4.11. There exists a zone near the surface with a thickness of $\sim 20 \mu m$ where the second phase particles appear brighter in contrast than the particles present below such zone and all through the bulk of the sample. The depth from the surface of this Fe-containing zone increases with aging time at a given temperature, reaching a maximum observed thickness of $\sim 100 \mu m$ on aging at 1550°C for the extended duration of 50 h. Analysis of the EDS spectra collected from such brighter particles, along with comparison of spectra collected from the more prevalent less bright particles present in the core of the sample, suggests that the second phase particles present along the surface layer are metallic Fe. Representative EDS spectra corresponding to the two different types of particles, along with quantitative analysis, are presented in Fig. 4.11. Furthermore, XRD patterns recorded from the surface before grinding/polishing confirm the absence of $FeAl_2O_4$ and the presence of metallic α -Fe as the second phase at the surface (see Fig. 4.11). Formation of similar layered Al_2O_3 -based composite microstructures containing $FeAl_2O_4$ as the secondary phase in the bulk and a surface layer containing metallic Fe has also been previously observed during spark plasma sintering in vacuum of $Al_2O_3 - 7 \text{ mol.}\% Fe_2O_3$ powders [13]. However in the cited work [13], the amount, size and distribution of the secondary phase particles were not studied.

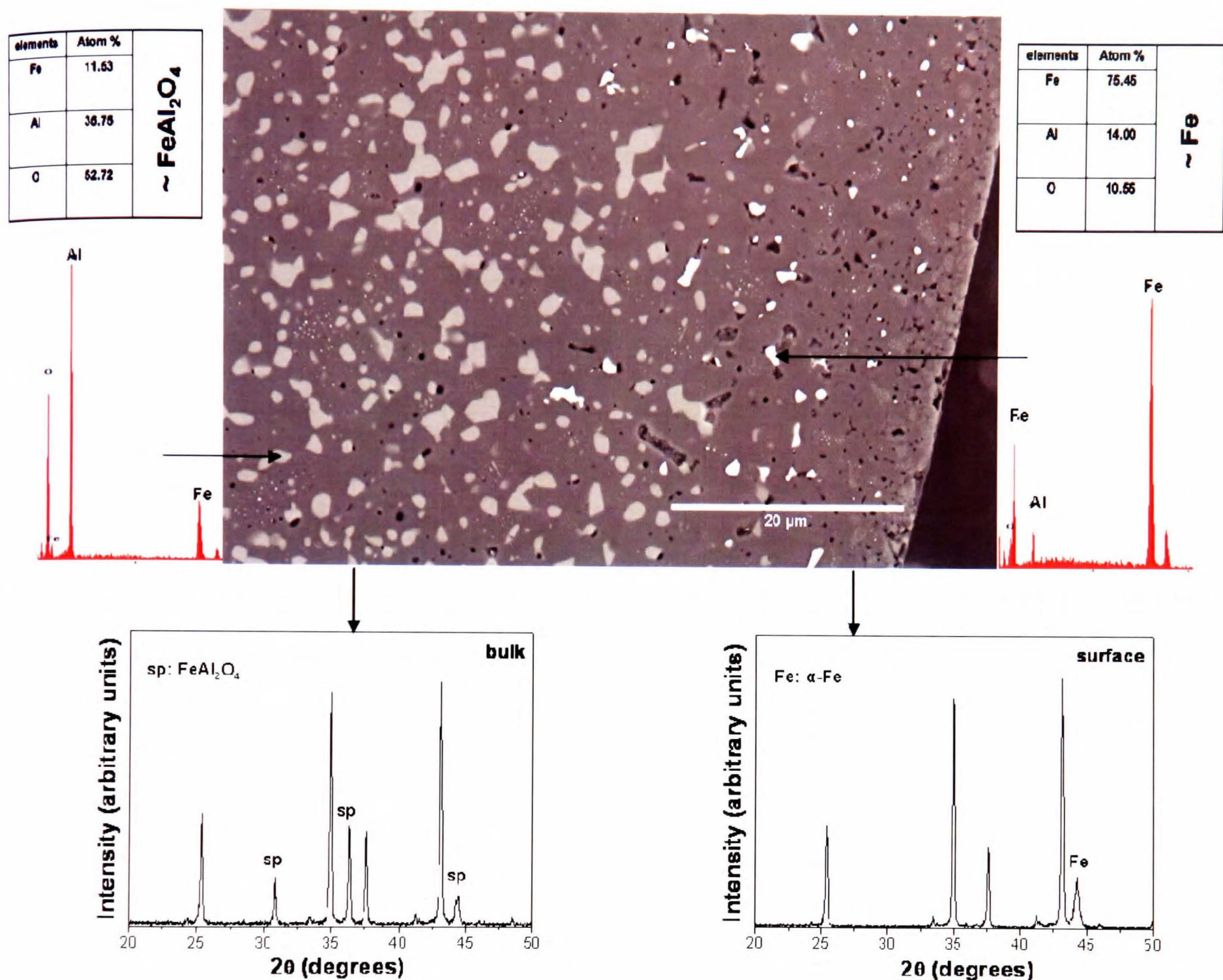


Fig. 4.11. BSE image of cross sectional view of as aged (1450°C; 20 h; N₂ + H₂) A10F sample, showing the presence of Fe as the secondary phase (brighter contrast) near the surface, as opposed to FeAl₂O₄ at the bulk. EDX spectra obtained from the respective secondary phases, along with XRD patterns collected from the surface (before grinding) and the bulk (after grinding/polishing), confirm the presence of α-Fe and the absence of FeAl₂O₄ at the surface of the aged samples.

4.1.2. Mechanical Properties of the Al_2O_3 - FeAl_2O_4 Nanocomposites

4.1.2.1. Vickers Hardness and Indentation Fracture Toughness

The room temperature hardness (H_v) and indentation fracture toughness (K_{Ic}), as obtained via Vickers indentation (load: 5 kg), are reported in Table 4.3. It can be observed that the samples developed on reduction aging at 1450°C for 0 - 20 h possessed hardness between 18-19 GPa, which are comparable to that of pure Al_2O_3 (~ 20 GPa) and slightly improved with respect to that of A10F solid solution (~ 17 GPa). However, hardness of the 'composite' aged for 50 h (~ 17 GPa) appears to be slightly less than that of pure Al_2O_3 and the 'nanocomposites' developed by aging for shorter duration. It must be noted that considering the relatively large scatter in the hardness values measured for the 'composite', it is difficult to specifically state that the hardness decreases with increase in aging time at 1450°C . With respect to the samples aged at 1550°C , the values reported in Table 4.4 indicate that the hardness was considerably reduced on aging at the higher temperature. However, due to the presence of extensive pull outs on the as 'polished surfaces' (see section 4.1.1.2.2) the Vickers hardness of these samples could not be measured very accurately, especially for the samples aged for longer durations (> 10 h).

An important observation that can be made from SEM images of the Vickers indents is that although monolithic Al_2O_3 exhibits pronounced radial cracking (Fig. 4.12a), the lengths of the cracks are less for the nanocomposites (Fig. 4.12b). A closer look at the paths of the Vickers indentation induced cracks reveals that the cracks are deflected around the coarser (Fig. 4.12c,d), as well as the nanosized (Fig. 4.12e,f), second phase particles. In fact, as reported in Table 4.4, the nanocomposites developed for optimum durations of 15 and 20 h at 1450°C possessed considerably improved indentation toughness ($\sim 5 \text{ MPa m}^{1/2}$) with respect to that of monolithic Al_2O_3 ($\sim 3.5 \text{ MPa m}^{1/2}$)

and A10F solid solution ($\sim 3.8 \text{ MPa m}^{1/2}$). However for the samples aged at 1550°C , with due consideration to the unreliability in the reported K_{Ic} values due to the poorer surface finish (similar to the H_{V5} values), the improvement in indentation fracture toughness seems to be less pronounced.

Table 4.4. Vickers hardness (H_{V5}) and Indentation fracture toughness (K_{Ic}), as measured with 5 kg indentation load, for monolithic Al_2O_3 , A10F solid solution and nanocomposites developed by reduction aging of A10F at 1450°C and 1550°C for different durations (up to 50 h).

Materials	Vickers Hardness (H _{V5} ; GPa)	Indentation Fracture Toughness (K _{Ic} ; MPa m ^{1/2})	Vickers Hardness (H _{V5} ; GPa)	Indentation Fracture Toughness (K _{Ic} ; MPa m ^{1/2})
Monolithic Al ₂ O ₃ ; (as sintered; 1450°C; 5 h)	20.1 ± 0.4	3.5 ± 0.7		
A10F solid solution; (as sintered; 1450°C; 5 h)	17.1 ± 0.8	3.8 ± 0.3		
Aged samples	Aging temperature: 1450°C		Aging temperature: 1550°C	
Al ₂ O ₃ - FeAl ₂ O ₄ ; (aged in N ₂ + H ₂ for 0 h)	17.8 ± 0.3	3.6 ± 0.5	17.1 ± 0.4	4.1 ± 0.2
Al ₂ O ₃ - FeAl ₂ O ₄ ; (aged in N ₂ + H ₂ for 5 h)	17.7 ± 0.5	4.3 ± 0.8	16.8 ± 0.6	4.2 ± 1.1
Al ₂ O ₃ - FeAl ₂ O ₄ ; (aged in N ₂ + H ₂ for 10 h)	18.6 ± 0.2	4.8 ± 0.2	16.8 ± 0.2	4.1 ± 0.9
Al ₂ O ₃ - FeAl ₂ O ₄ ; (aged in N ₂ + H ₂ for 15 h)	18.8 ± 0.6	5.3 ± 0.7	16.2 ± 1.7	-
Al ₂ O ₃ - FeAl ₂ O ₄ ; (aged in N ₂ + H ₂ for 20 h)	18.4 ± 0.7	4.9 ± 0.3	15.6 ± 1.9	-
Al ₂ O ₃ - FeAl ₂ O ₄ ; (aged in N ₂ + H ₂ for 50 h)	16.9 ± 1.8	4.2 ± 0.8	-	-

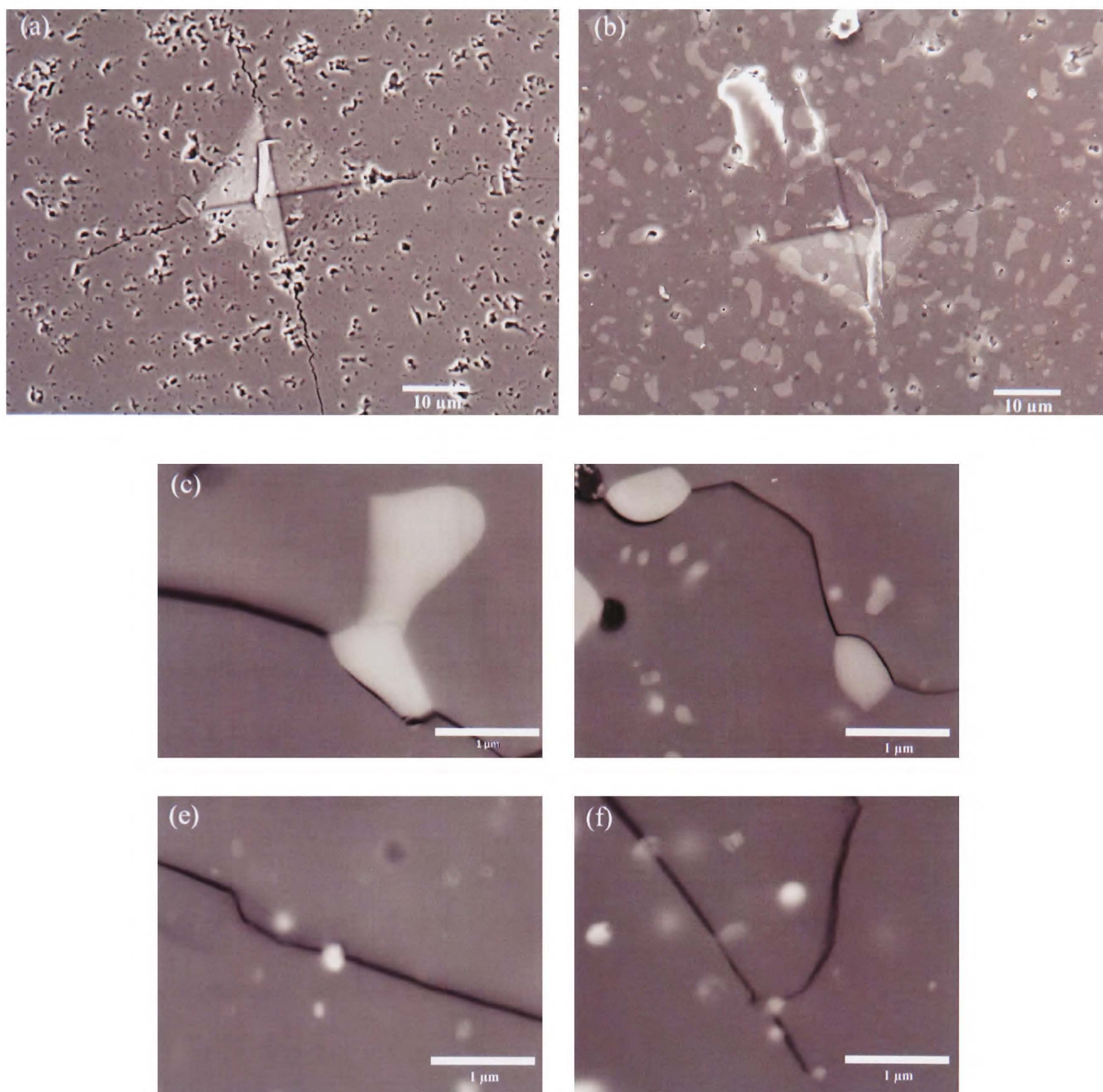


Fig. 4.12. SEM images of Vickers indents, as obtained with a maximum load of 5 kg on ground and polished surfaces of (a) pure Al_2O_3 (b) Al_2O_3 - FeAl_2O_4 nanocomposite developed on aging of A10F solid solution at 1450°C for 20 hrs in reducing atmosphere. Higher magnification BSE-SEM images of the Vickers indentation induced crack paths presents evidences of crack deflection by (c), (d) coarser micron sized and (e), (f) nanosized second phase particles.

4.1.2.2. Flexural Strength and SEVNB Fracture Toughness

The room temperature fracture toughness and flexural strength of the Al_2O_3 - FeAl_2O_4 micro/nanocomposites, developed on reduction aging of A10F solid solution at 1450°C are shown in Fig. 4.13. The surfaces subjected to tensile stresses during the 4-point bending experiments were ground and polished sufficiently to remove the Fe containing surface layers for all the specimens. While the as sintered A10F solid solution possessed similar fracture toughness and strength with respect to monolithic Al_2O_3 , most of the FeAl_2O_4 -containing Al_2O_3 materials possessed improved fracture toughness and strength with respect to pure Al_2O_3 . More precisely, the ‘hybrid micro/nano composites’ developed on aging for optimum durations of 10 - 20 h at 1450°C exhibited $\sim 40\%$ improvement in fracture toughness ($K_{Ic} \sim 4.5 \text{ MPa m}^{1/2}$) and $\sim 50\%$ improvement in flexural strength ($\sigma_f \sim 500 \text{ MPa}$) with respect to monolithic Al_2O_3 ($K_{Ic} \sim 3.1 \text{ MPa m}^{1/2}$; $\sigma_f \sim 350 \text{ MPa}$). However, the fracture properties of the composites developed without holding (0 h) at the aging temperature of 1450°C showed only a small improvement compared to monolithic Al_2O_3 . Furthermore, deterioration of the properties, in particularly the flexural strength, also resulted on aging for the extended duration of 50 h.

It must be noted that the variation with aging duration of the fracture toughness values, as measured via SEVNB technique, agrees with those measured using the indentation crack length measurement technique (see Table 4.3 and Fig. 4.13a) for the samples aged at 1450°C . However, the indentation method seems to marginally overestimate some of the fracture toughness values, with respect to those measured using the more conventional SEVNB technique.

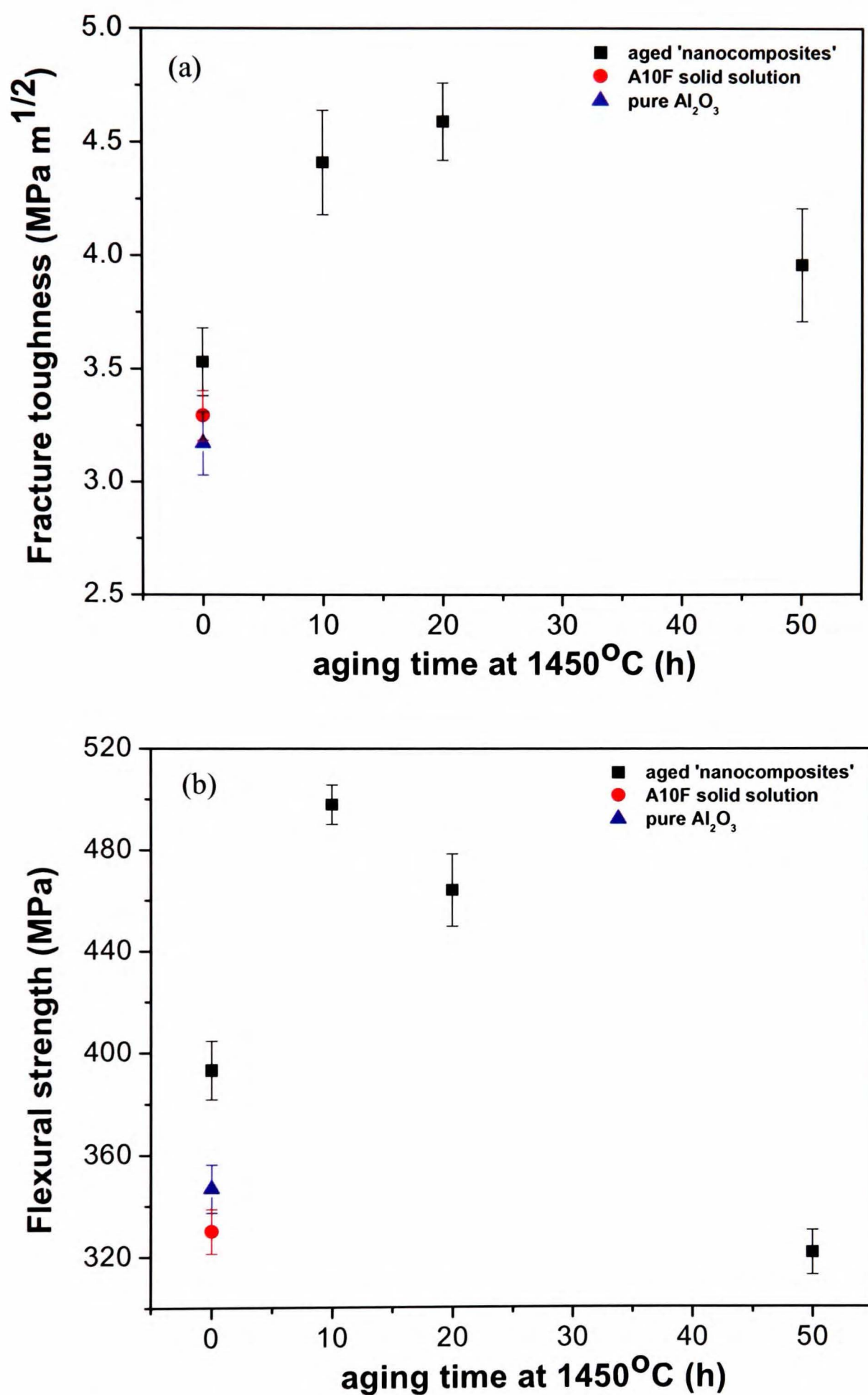


Fig. 4.13. Room temperature (a) fracture toughness, as measured by SEVNB technique and (b) flexural strength, as determined from 4-point bending, for monolithic Al₂O₃, A10F solid solution and the Al₂O₃ - FeAl₂O₄ composites/nanocomposites developed after reduction aging of A10F solid solution for different durations (0 - 50 h) at 1450°C.

4.1.2.3. Observation of Fracture Surfaces

SEM images corresponding to the fractured surfaces obtained during fracture toughness testing (SEVNB) of as sintered monolithic Al_2O_3 , A10F solid solution and the nanocomposites developed via reduction aging are presented in Fig. 4.14. It can be observed that monolithic Al_2O_3 (Fig. 4.14a), A10F solid solution (Fig. 4.14b), as well as the composite developed on reduction aging for 0 h (Fig. 4.14c) exhibited the classical almost completely intergranular mode of fracture. By contrast, the fracture mode changed to almost purely transgranular fracture on aging for 10 h or more at 1450°C (Fig. 4.14d,e). Another observation that can be made from the higher magnification BSE image obtained from the fractured surface of the nanocomposite aged for 20 h (Fig. 4.17f), is that although the intragranular nanosized particles appear to remain intact within the matrix upon fracture, the coarser inter granular particles seem to have fallen out during the fracture process. It can also be critically noted that the transgranular fracture surfaces are not planar cleavage planes, but contain a few step like features. Such step like features can also be observed on the transgranular fracture surfaces of Al_2O_3 - SiC nanocomposites containing intragranular SiC nano particles [14-17].

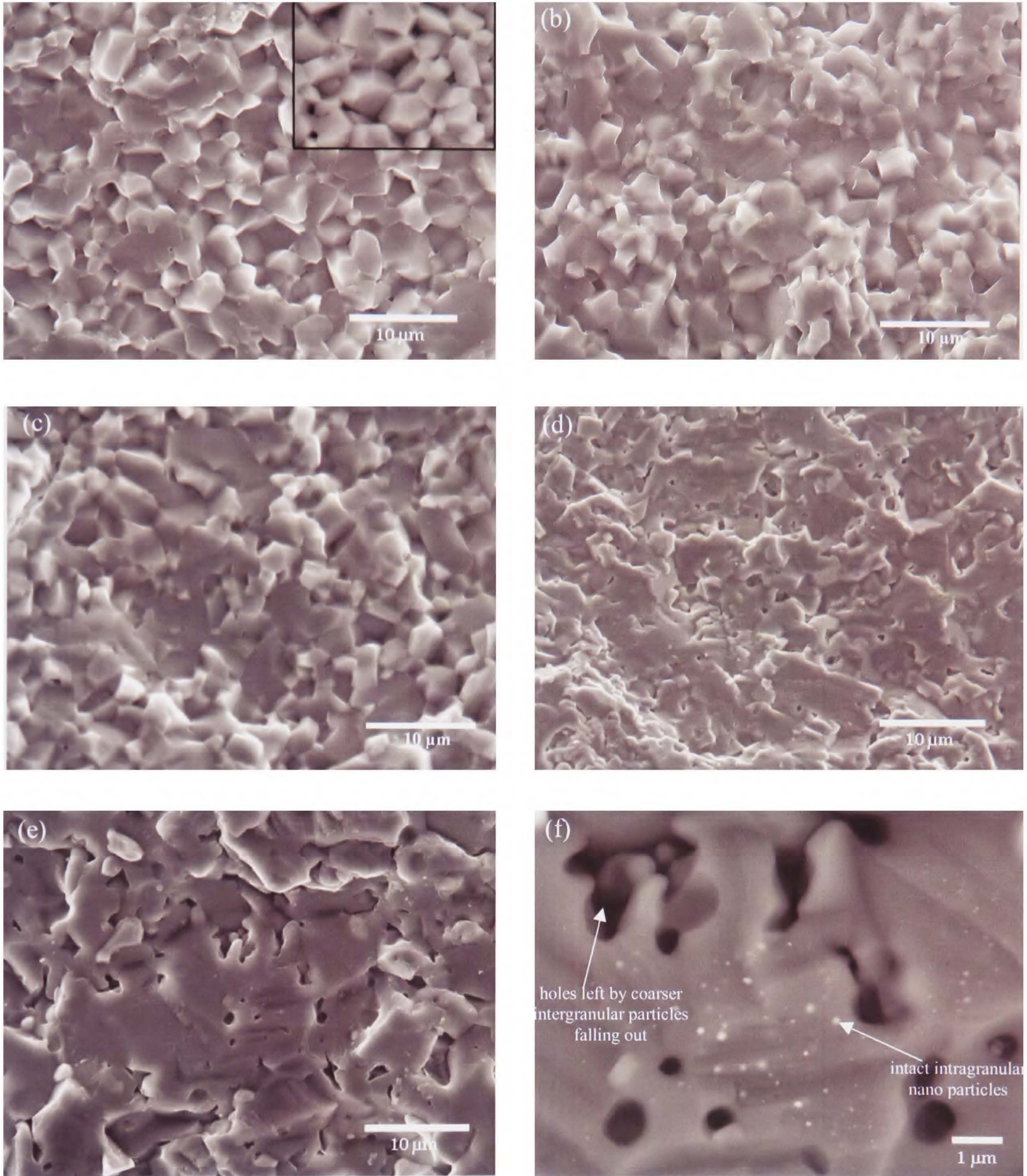


Fig. 4.14. SEM images of fractured surfaces obtained during fracture toughness testing (SEVNB) of (a) monolithic Al_2O_3 ; (b) as sintered A10F solid solution; Al_2O_3 - FeAl_2O_4 nanocomposite developed by reduction aging of A10F solid solution at 1450°C for (c) 0 hrs; (d) 10 hrs; (e) 20 hrs; and (f) higher magnification BSE-SEM image of fractured surface of nanocomposite (aged; 1450°C ; 20 h).

4.2. Discussion

4.2.1. Progress of Precipitation Reaction

Assuming that all the Fe comes out of solid solution as FeAl_2O_4 , the maximum volume percent of FeAl_2O_4 that can be theoretically produced by reduction aging of the A10F solid solutions is 21 %. As can be inferred from the investigations of the progress of the precipitation reaction via both the methods (Figs. 4.2b, 4.9) and the microstructural developments, the kinetics is significantly slower at the temperatures below 1450°C , which neither allows the reaction to go to completion (maximum FeAl_2O_4 formed ~ 6 vol.% at 1250°C and ~ 14 vol.% at 1350°C), nor leads to the formation of the intra granular particles even after aging for the extended duration of 50 h. On the contrary, the precipitation reaction goes to completion after 10-15 h during aging at the higher temperatures of 1450°C and 1550°C (FeAl_2O_4 precipitated ~ 20 vol.%), with nanosized intra granular particles appearing after ~ 10 h. Considering that grain boundary diffusion co-efficients are higher with respect to bulk diffusion co-efficients it is not surprising that the incubation period for precipitation of intra granular particles is higher as compared to the formation of the second phase particles along the matrix grain boundaries. It must be noted that to the best of the authors' knowledge the development of oxide-oxide nanocomposites, containing such high volume fractions of second phase particles (up to ~ 20 vol.%), via similar aging technique, has not been reported previously. Furthermore, development of dense Al_2O_3 - SiC nanocomposites via pressureless sintering has been achieved only for nanocomposites containing a maximum of 5 vol.% SiC particles [18], and only on sintering at a higher temperature.

Assuming that the precipitation reaction is controlled by the diffusion of the various species, the reaction rate (r), which is inversely proportional to the time taken (t) for

completing a certain fraction of the reaction, can be expressed according to the Arrhenius equation as;

$$r = 1/t = A.\exp(-Q/RT) \quad (4.1)$$

$$\Rightarrow t_1 / t_2 = \exp(-Q/RT_1) / \exp(-Q/RT_2) \quad (4.2)$$

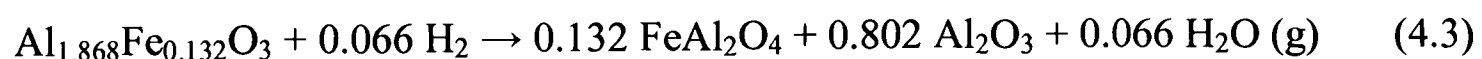
where Q is the activation energy for the rate controlling step, R is the gas constant (8.314 J/mol/K) and T is the temperature. The times (say t_1 and t_2) taken at the different temperatures (say T_1 and T_2) for completion of a certain fraction of the precipitation reaction have been measured at different points along the progress of the reaction from the plots in Figs. 4.2b and 4.9. The measured times, along with the corresponding temperatures, have been used to determine the activation energy for the precipitation reaction based on eq. (2). Such estimated activation energies have been found to vary between 270 and 330 kJ/mol. However, considering that in the literature base, values ranging from 200 - 700 kJ/mol and 200 - 500 kJ/mol have been reported for the activation energies of lattice self diffusion of oxygen and aluminium, respectively, in alumina [19-21], it is difficult to identify the rate limiting species based on the above estimation. Furthermore, Halloran and Bowen [22] reported a value of $Q \sim 273$ kJ/mol for Fe diffusion in FeAl_2O_4 in reducing atmosphere (CO_2/CO).

4.2.2. Overall Chemical Reactions Responsible for FeAl_2O_4 and Fe Phase Evolutions

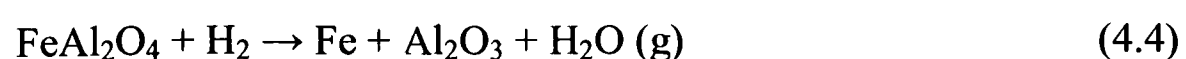
The present processing scheme, which involves aging in the presence of H_2 as the reducing agent, leads to changes in the chemical composition of the starting materials (solid solution of Fe_2O_3 in Al_2O_3) to result in the formation of new phases (FeAl_2O_4

and Fe). With regard to the formation of metallic Fe at the surface layer, it has been observed that the depth from the surface of the Fe containing zone increased with aging time at a given temperature. These surface layers contained hardly any FeAl_2O_4 particles. This suggests that the as precipitated FeAl_2O_4 particles get further reduced to metallic Fe progressively from the surface during continued aging. Furthermore, TEM observations of foils developed from near the surface regions of the as aged composites revealed that some portions of some of the second phase particles possess different contrasts, with respect to the other regions of the same particles, when tilted at various orientations with respect to the incident beam (Fig. 4.15a,b). CBED patterns obtained from these portions can be indexed in terms of $\alpha\text{-Fe}$ (Fig. 4.15b). It is believed that the presence of metallic Fe in a portion of the second phase particles is evidence that particles present near the surface, which were initially precipitated as FeAl_2O_4 , subsequently get transformed to Fe. Such partially transformed FeAl_2O_4 particles (to Fe), present near the interface of the Fe-containing surface layer and the bulk, can also be observed on BSE micrographs obtained from the cross sections (Fig. 4.16a,b).

The following basic chemical reactions are proposed to account for the overall phase evolutions along the bulk of the samples, as well as at the surface layers. The initial composition corresponding to the solid solution of 10 wt.% Fe_2O_3 in Al_2O_3 can be represented by $\text{Al}_{1.868}\text{Fe}_{0.132}\text{O}_3$. Considering that FeAl_2O_4 is formed as the second phase throughout the bulk of the samples on reduction aging;



reaction (4.3) is supposed to have the major contribution. At the surfaces the FeAl_2O_4 gets further reduced to metallic Fe. The following reaction is believed to account for such additional reduction step;



It can be observed that both the reactions lead to the removal of O^{2-} which should result in mass loss during aging. The theoretical mass loss accompanying reaction 4.3 is estimated to be $\sim 0.998\%$, while reaction 4.4 should result in an additional mass loss of $\sim 1.996\%$. The overall mass loss after reduction aging for different time-temperature schedules will depend on the extent of both the reactions taking place for the respective schedules. The extent of the overall reaction 4.3 after aging for different durations at 1450°C has been estimated based on the relative change in interplanar spacing at the respective aging times with respect to that after 20 hrs, when the precipitation reaction is believed to have reached equilibrium (see Fig. 4.2b). The depth of the zones from the surface corresponding to the formation of metallic Fe (due to reaction 4.4) has been noted for the different aging schedules, which allows the estimation of the mass loss resulting from the additional occurrence of reaction 4.4 at such surface layers. The net mass losses due to occurrence of reaction 4.3 throughout the samples, along with the additional contribution from reaction 4.4 at the surface, have been estimated for all the aging durations at the optimum aging temperature of 1450°C . As presented in Fig. 4.17, such estimations have been found to correlate well with the experimentally measured mass losses for the different aging durations, supporting the validity of equations (4.3) and (4.4).

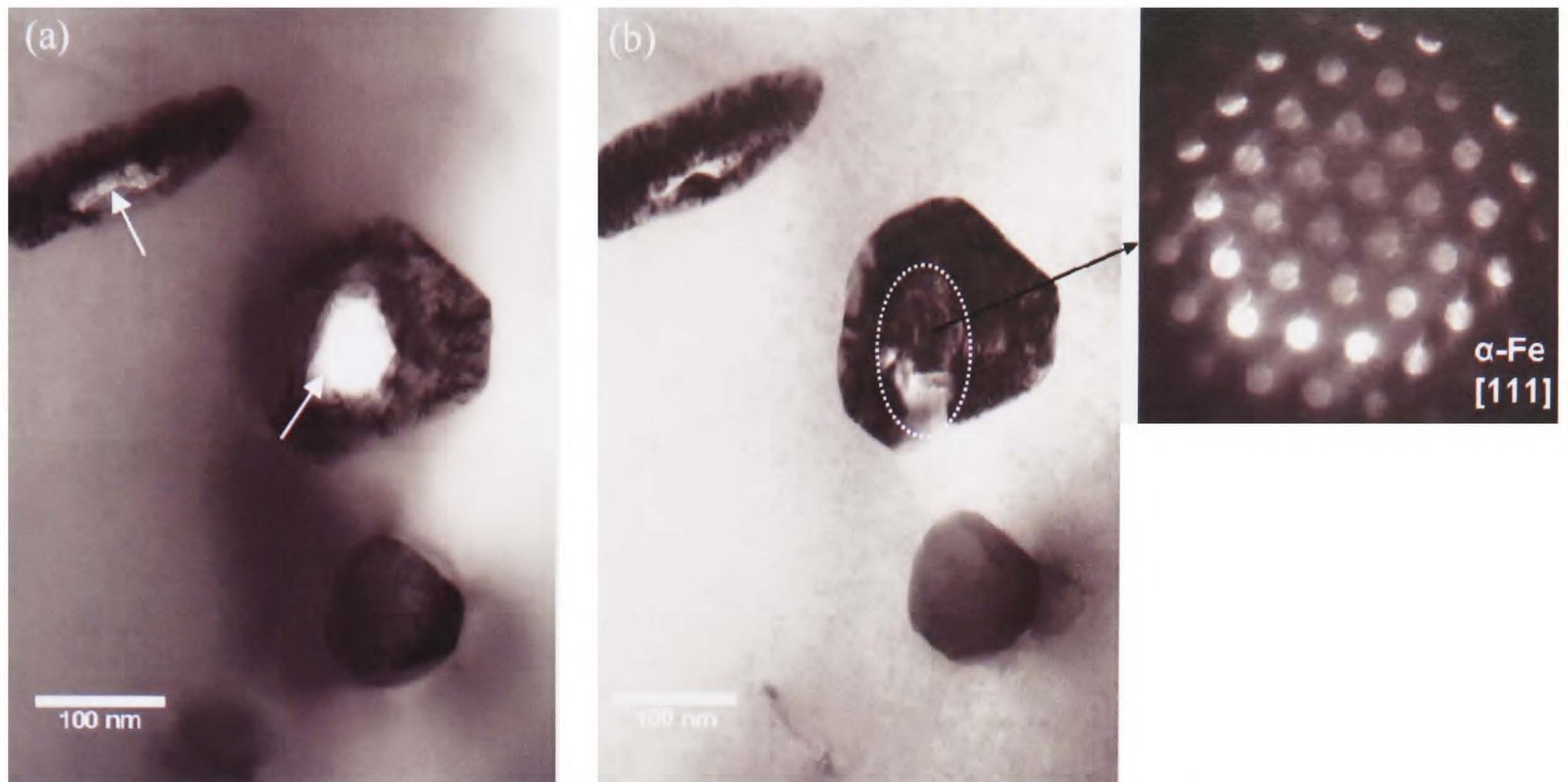


Fig. 4.15. (a) TEM image, as obtained with foil prepared from near the surface of aged A10F (1450°C; 20 h; N₂ + H₂), showing the presence of a different phase (having brighter contrast) at some portion the secondary phase particles (indicated with arrows). (b) CBED pattern obtained from the small region corresponding to the different phase can be indexed in terms of α-Fe.

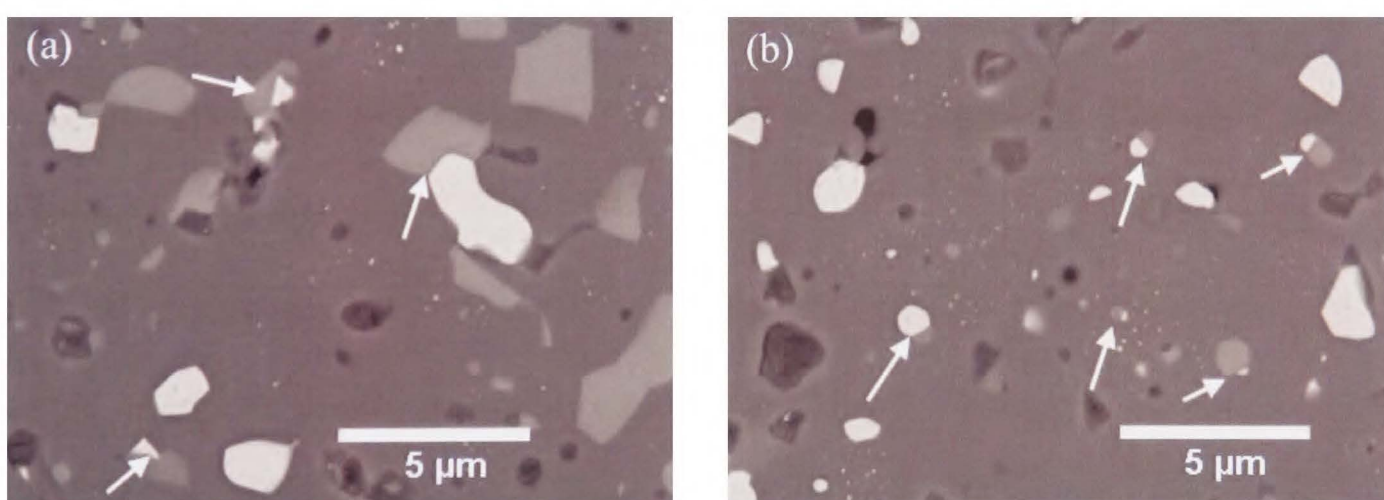


Fig. 4.16. (a) and (b) BSE-SEM images obtained from near the interface of the Fe-containing surface layer and the FeAl₂O₄ containing bulk show the presence of FeAl₂O₄ particles being partially transformed to Fe (brighter portion). Such particles are indicated with arrows.

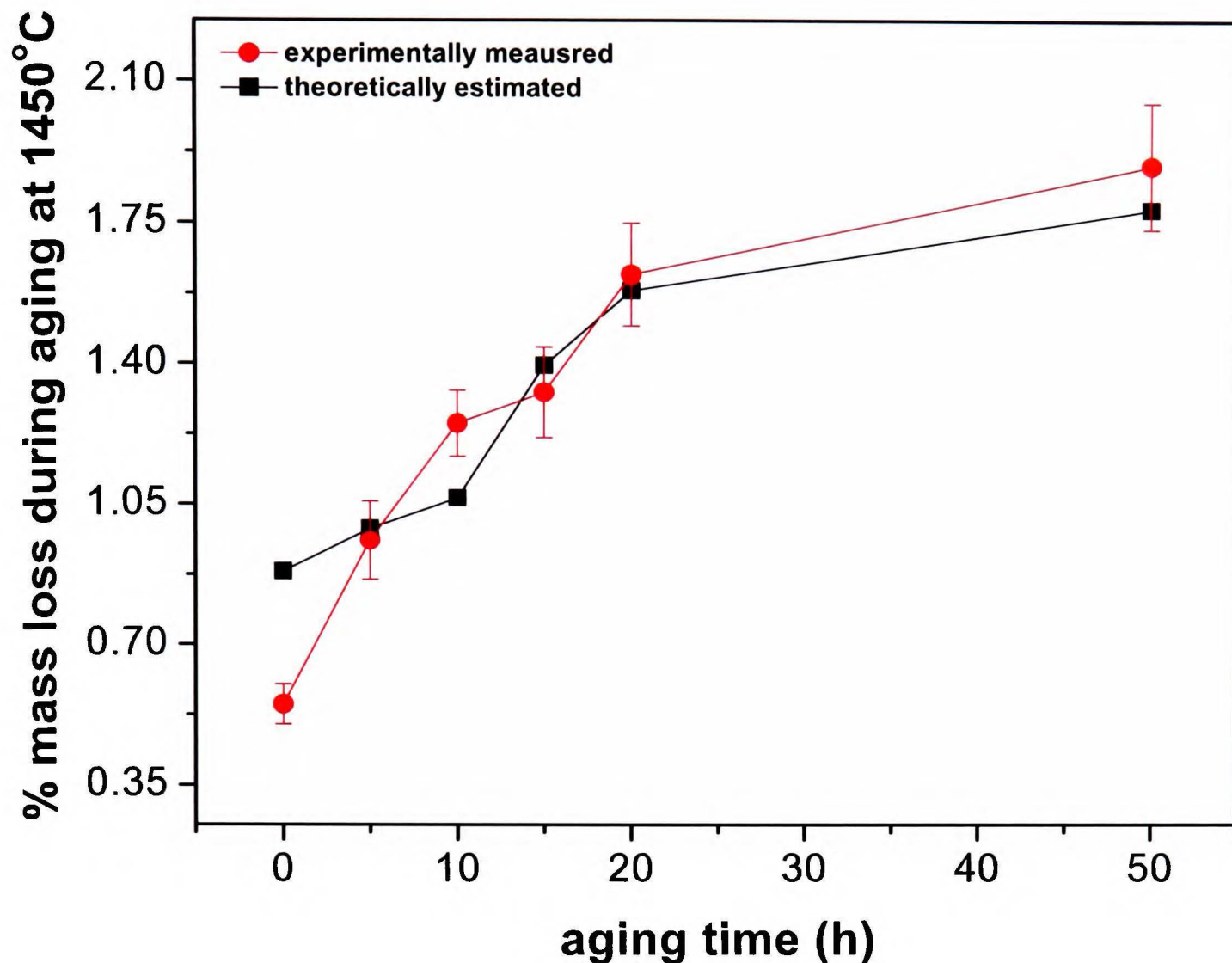


Fig. 4.17. Comparison of the experimentally measured and theoretically estimated mass loss as a function of aging time (0 - 50 h) during reduction aging of A10F solid solutions at 1450°C.

4.2.3. Correlation between Microstructural Development, Fracture mode and Mechanical properties

Critical assessment of the observed variation of the fracture properties with reduction aging duration points towards some correlations between the aging duration, microstructural development (volume fraction, size and distribution of the second phase particles), fracture mode and the strength/fracture toughness for the as developed composites (Figs. 4.6, 4.13 and 4.14). It has been observed that incorporation of Fe as solid solution, as well as precipitation of a limited amount of micron sized FeAl_2O_4 particles along the matrix grain boundaries and triple point

corners (on aging at 1450°C for 0 h) does not change the fracture mode from intergranular to transgranular. At the same time, such solution treatment and aging treatment does not lead to any obvious improvement in the fracture properties. By contrast, aging for longer periods (≥ 10 h) resulted in the precipitation of nanosized second phase particles within the matrix grains, and concomitantly leads to significant improvement in the fracture toughness, as measured via SEVNB (see Fig. 4.13a) as well as Vickers indentation (see Table 4.3), and flexural strength (see Fig. 4.13b). It must be noted here that such precipitation of nano-sized second phase particles within the matrix grains also coincides with the change in fracture mode to purely transgranular for the nanocomposites. These observations point towards some interplay between the change in fracture mode and the improvement in fracture toughness and strength of the nanocomposites. However, on continued aging for 50 h, the fracture toughness for the composites deteriorated to a relatively modest extent, accompanied by drastic reduction in the experimentally measured flexural strength. The formation of an extremely coarse and nearly interconnected network of intergranular particles on aging for such extended duration (Fig. 4.6d) might have such a degenerating influence on the fracture properties. In fact, it has been observed that such coarser intergranular particles tend to get pulled out during metallographic polishing (Fig. 4.6d and 4.7). Furthermore, such particles even tend to fall out from the matrix during fracture (Fig. 4.14f). It must also be noted that due to extensive pull-out of the coarser particles during metallographic polishing of the tensile surfaces of the bend specimens, poorer surface finish might have contributed partly towards the much lower value of the flexural strength measured using 4-point bending of the Al_2O_3 - FeAl_2O_4 composite samples developed on reduction aging for the extended

duration of 50 h at 1450°C. The reasons behind such deleterious effects of the coarser intergranular particles will be discussed in detail in the next chapter.

4.2.4. Toughening Mechanisms in the Al₂O₃ - FeAl₂O₄ Nanocomposites

The different mechanisms which have been reported to result in improved fracture toughness for particulate reinforced ceramic composites and nanocomposites can be broadly classified as; (a) residual stress (strain) field due to co-efficients of thermal expansion (α) mismatch between the ceramic matrix and the particulates [23-25]; (b) change in fracture mode from intergranular to transgranular [17,23,25-27]; (c) micro/nano cracking in the frontal process zone ahead of the main crack tip [17]; (d) crack bridging by the reinforcing second phase particles [23,24] and (e) crack deflection by the particulates ahead of the propagating crack [23,24,28]. The possible contributions of different toughening mechanisms towards the improvement in the mechanical properties of the present Al₂O₃ - FeAl₂O₄ nanocomposites developed at the optimum aging conditions are discussed in the following.

In the nanocomposites under investigation, the second phase particles (FeAl₂O₄) have higher thermal expansion co-efficient ($\alpha_p \sim 13 \times 10^{-6} \text{ K}^{-1}$ [29]) with respect to that of the matrix (Al₂O₃; $\alpha_m \sim 8 \times 10^{-6} \text{ K}^{-1}$ [29,30]). Such mismatch in co-efficients of thermal expansion is likely to result in the development of residual compressive stresses in the matrix during cooling from the heat treatment temperatures. According to a theory proposed by Taya et al. [24], development of such compressive residual stresses in the matrix can result in the toughening of particulate reinforced ceramic composites.

The model [24] is based on the misfit strain (ε) that gets developed in the particles due to the co-efficient of thermal expansion (CTE) mismatch and which is given by,

$$\varepsilon = \int_{T_p}^{T_R} (\alpha_p - \alpha_m) dT \quad (4.5)$$

where T_p is the temperature below which plasticity is considered to be negligible $\sim 1000^\circ\text{C}$ and T_R is room temperature. The isotropic average stress fields in the particles and matrix are given by $\langle\sigma\rangle_p$ and $\langle\sigma\rangle_m$, respectively, which are defined for a given volume fraction of second phase particles (f_p) according to the following equations;

$$\frac{\langle\sigma\rangle_p}{E_m} = \frac{-2(1-f_p)\beta\varepsilon}{A} \quad (4.6)$$

and

$$\frac{\langle\sigma\rangle_m}{E_m} = \frac{2f_p\beta\varepsilon}{A} \quad (4.7)$$

where,

$$A = (1-f_p)(\beta+2)(1+\nu_m) + 3\beta f_p(1-\nu_m) \quad (4.8)$$

$$\beta = \left(\frac{1+\nu_m}{1+\nu_p} \right) \left(\frac{E_p}{E_m} \right) \quad (4.9)$$

where, ν_m and E_m are the Poisson's ratio (~ 0.2) and elastic modulus (~ 350 GPa) of the matrix (Al_2O_3) [31], ν_p and E_p are the Poisson's ratio (~ 0.3) and elastic modulus (~ 225 GPa) of the second phase particles (FeAl_2O_4) [32,33].

In the case of the composite developed on aging for 0 h at 1450°C , considering f_p as 0.1 (see Fig. 4.9) and using eqs. 4.5 - 4.9, the residual stress in the matrix can be estimated as; $\langle\sigma\rangle_m = -143.5$ MPa. It may be recalled here that this composite contains only intergranular micron sized second phase particles (see Fig. 4.6a). According to Taya et al [24], the existence of such compressive residual stresses in the matrix of particulate reinforced composites, decreases the stress intensity factor and hence increase the fracture toughness (K_{Ic}) by ΔK_I , which is given by;

$$\Delta K_I = 2 \langle \sigma \rangle_m \sqrt{\frac{2(\lambda - d)}{\pi}} \quad (4.10)$$

where λ is the interparticle distance and d is the average diameter of the second phase particles. Considering λ as 4 μm (see Fig. 4.6a) and d as 1 μm (see Table 4.1) for the composite developed on aging for 0 h, eq. (4.10) predicts a fracture toughness increase by $\sim 0.4 \text{ MPa m}^{1/2}$; which agrees reasonably well with the experimentally measured (via SEVNB) fracture toughness increment of $\sim 0.3 \text{ MPa m}^{1/2}$ over that of monolithic Al_2O_3 (see Fig. 4.13a). Hence for the composite developed on aging for a duration of 0 h and characterized by the presence of only intergranular second phase particles, the modest toughening effect due to the presence of thermal expansion coefficient mismatch induced residual stress seems to be the major contributor.

It may be recalled here that on aging for longer durations ($> 10 \text{ h}$) at 1450°C nanosized intragranular particles were precipitated in addition to the presence of the coarser intergranular particles (see section 4.1.1.2.2). Such microstructural development was also accompanied by considerable increment in fracture toughness (see section 4.1.1.2.2). Additional contribution towards such residual stress induced toughening solely by the nanosized intragranular particles (volume fraction ~ 0.9), in the nanocomposite developed on aging for a duration of 20 h, has been estimated to be $\sim 0.2 \text{ MPa m}^{1/2}$ using eqs. 4.5 - 4.10. Hence, toughening based on thermal expansion mismatch induced residual stresses alone cannot account for the experimentally observed fracture toughness increment by $\sim 1.4 \text{ MPa m}^{1/2}$ for the inter/intragranular nanocomposite. Hence, some additional toughening mechanisms must be operative in the presence of nanosized intragranular particles.

Among the present evidences for possible toughening mechanisms, the change in fracture mode from intergranular (for monolithic Al_2O_3 , A10F solid solution and the

intergranular particle reinforced Al_2O_3 - FeAl_2O_4 composite developed on reduction aging for 0 h) to transgranular for the nanocomposites seems to coincide with the appearance of the nanosized intragranular particles during reduction aging (see section 4.2.3). Hence, the change in fracture mode may account partly for the considerable improvement in fracture toughness in the presence of such intragranular nano FeAl_2O_4 particles. It must be mentioned here that, based on the relative specific surface energies for grain boundary fracture and transgranular fracture in alumina, Hansson and co workers [34] have estimated that a change in fracture mode from intergranular to transgranular fracture in alumina can lead to an increase in the fracture toughness of 30-50%, which is sufficient to account for at least the majority of the net 40% toughness increase experimentally observed for the nanocomposite developed on aging for 20 h. Hence, the above discussion suggests that, among the various possible toughening mechanisms, residual stress induced by CTE mismatch and change in fracture mode from intergranular to transgranular in the presence of the second phase particles are the major contributors towards the improvement in fracture toughness for the Al_2O_3 - FeAl_2O_4 nanocomposites developed by reduction aging of A10F solid solutions.

4.3. Summary and Outlook

The present results demonstrate for the first time the formation of an effective alumina-based “nanocomposite” with significantly improved mechanical properties relative to monolithic alumina by in situ solid state precipitation of an intragranular nano-particulate second phase (FeAl_2O_4) within an alumina matrix. Of fundamental

interest are the ability to produce uniform, agglomerate-free dispersions of extremely fine nanoparticles, that cannot be produced by the conventional mixed powder processing route, and the fact that the intragranular nanoparticles are shown to be essential to the property improvements reported. Given that the commercial application of the promising ceramic-based nanocomposites are severely hindered by processing difficulties, such as requirement of commercially undesirable sintering techniques or requirement of ultra fine sized starting powders, the report excites new opportunities for the development of high performance ceramic nanocomposites via cost effective processing routes.

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Chapter 5

WEAR RESISTANCE OF Al_2O_3 -BASED PARTICULATE NANOCOMPOSITES

Among the different properties of Al_2O_3 -based ceramics that are reported to be improved upon reinforcement with nanosized second phase particles, probably the most remarkable and reproducible improvements have been achieved for the tribological properties [1-10]. To be precise, Al_2O_3 -SiC particulate nanocomposites, characterized by the presence of nanosized SiC particles within the matrix grains and sub micron SiC particles along the grain boundaries, have been reported to possess improved wear resistance as compared to monolithic alumina by a factor of ~ 3 [1,2,9,10]. In this light, we report here the results of our present investigations on the abrasive wear behaviour of the novel Al_2O_3 - FeAl_2O_4 nanocomposites, developed via aging of Al_2O_3 - 10 wt.% Fe_2O_3 solid solutions in reducing atmosphere ($\text{N}_2 + 4\% \text{H}_2$) at 1450°C and 1550°C for durations of 0, 10 and 20 h, which were described in chapter 4.

5.1. Results

5.1.1. Wear Rates

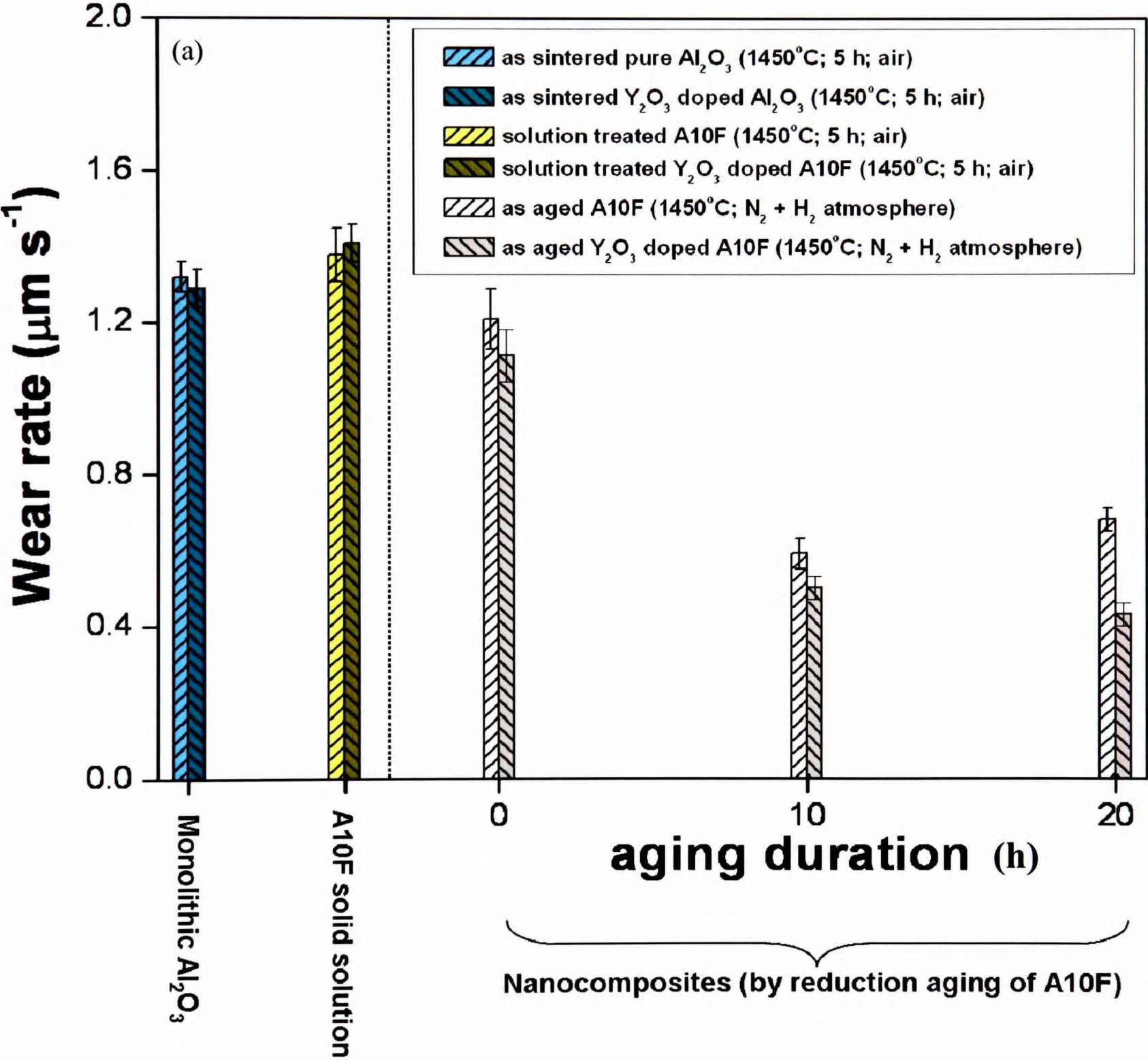
A comparison of the abrasive wear rates, as measured for monolithic alumina, Al_2O_3 - Fe_2O_3 solid solutions and the Al_2O_3 - FeAl_2O_4 nanocomposites developed on reduction aging at 1450°C , both in the presence and absence of yttria (~ 250 ppm) is presented in Fig. 5.1a. The wear rates, as quoted here, can be interpreted as the rates at which the material got removed (by volume) per unit contact area per unit time by abrasion against diamond particles (45 μm diamond slurry), as described in section 3.4 of chapter 3.

It can be observed that the incorporation of Fe_2O_3 in solid solution resulted in a slight increase in the wear rate over that of monolithic Al_2O_3 . The addition of ~ 250 ppm of

yttria did not affect the wear rates for either monolithic alumina or the solid solution to any notable degree. Probably the most important result of the present investigation is that the Al_2O_3 - FeAl_2O_4 nanocomposites, developed on reduction aging of the Al_2O_3 - Fe_2O_3 solid solutions for 10 and 20 h, exhibited considerably reduced wear rates as compared to that of Al_2O_3 and the solid solutions. Additionally, doping with just ~ 250 ppm of Y_2O_3 resulted in further lowering of the wear rates for these nanocomposites. However, aging for 0 h at 1450°C (where 0 h means that the specimen was heated to the specific temperature and cooled again without holding) resulted in only a small improvement in the wear resistance, even in the presence of yttria. It can also be observed that in the absence of yttria, the nanocomposite developed by aging for 10 h exhibited the least wear rate, as compared to those aged for 0 and 20 h. On the contrary, with yttria doping, the wear rate decreased monotonically with increase in the aging duration up to 20 h. In other words, Y_2O_3 doping had the maximum influence on the wear resistance of the nanocomposite developed by aging for 20 h at 1450°C (by a factor of ~ 1.6 , compared with the corresponding specimen without yttria). This nanocomposite exhibited an average wear rate of $\sim 0.45 \mu\text{m/s}$, as against the wear rate of $\sim 1.25 \mu\text{m/s}$ recorded with monolithic alumina of similar grain size. It must be mentioned here that the wear rate obtained for monolithic alumina in this study is comparable with the abrasive wear rates reported earlier for monolithic alumina possessing similar grain sizes using the same test [1,2]. Hence, the results of the present abrasive wear tests reveal that the Y_2O_3 doped Al_2O_3 - FeAl_2O_4 nanocomposites developed at optimum aging conditions (1450°C ; 20 h) possess significantly enhanced wear resistance (by a factor of ~ 2.5) as compared to that of monolithic Al_2O_3 . This improvement in abrasive wear resistance for Al_2O_3 - FeAl_2O_4 nanocomposites over that of monolithic Al_2O_3 is only slightly

inferior to the maximum improvement (by a factor of ~ 3.4) reported earlier for Al_2O_3 -SiC nanocomposites when measured following the same experimental procedure [1,2].

Fig. 5.1b presents the wear rates obtained with the nanocomposites developed at the higher reduction aging temperature of 1550°C . For comparison, the wear rates recorded with the nanocomposites at the lower aging temperature (1450°C) are also presented. From the comparative plot, it is quite obvious that the nanocomposites developed at the higher aging temperature possessed inferior wear resistance with respect to those developed by aging at 1450°C . Additionally, unlike for the nanocomposites developed at 1450°C , no significant variation in the wear rates with aging time could be seen within the limits of the experimental error. The wear rates in the absence of yttria doping varied between $1.2\ \mu\text{m/s}$ to $1.3\ \mu\text{m/s}$, which are similar to those recorded with monolithic alumina. Hence, the nanocomposites developed by aging at 1550°C do not possess considerably improved wear resistance with respect to pure Al_2O_3 . It can be further observed from Fig. 5.1b that yttria doping apparently improved the wear resistance only for the nanocomposite developed on aging for 0 h, and then only by a small amount. However, the wear rates for the nanocomposites developed after 10 and 20 h of aging were not affected by the presence of Y_2O_3 .



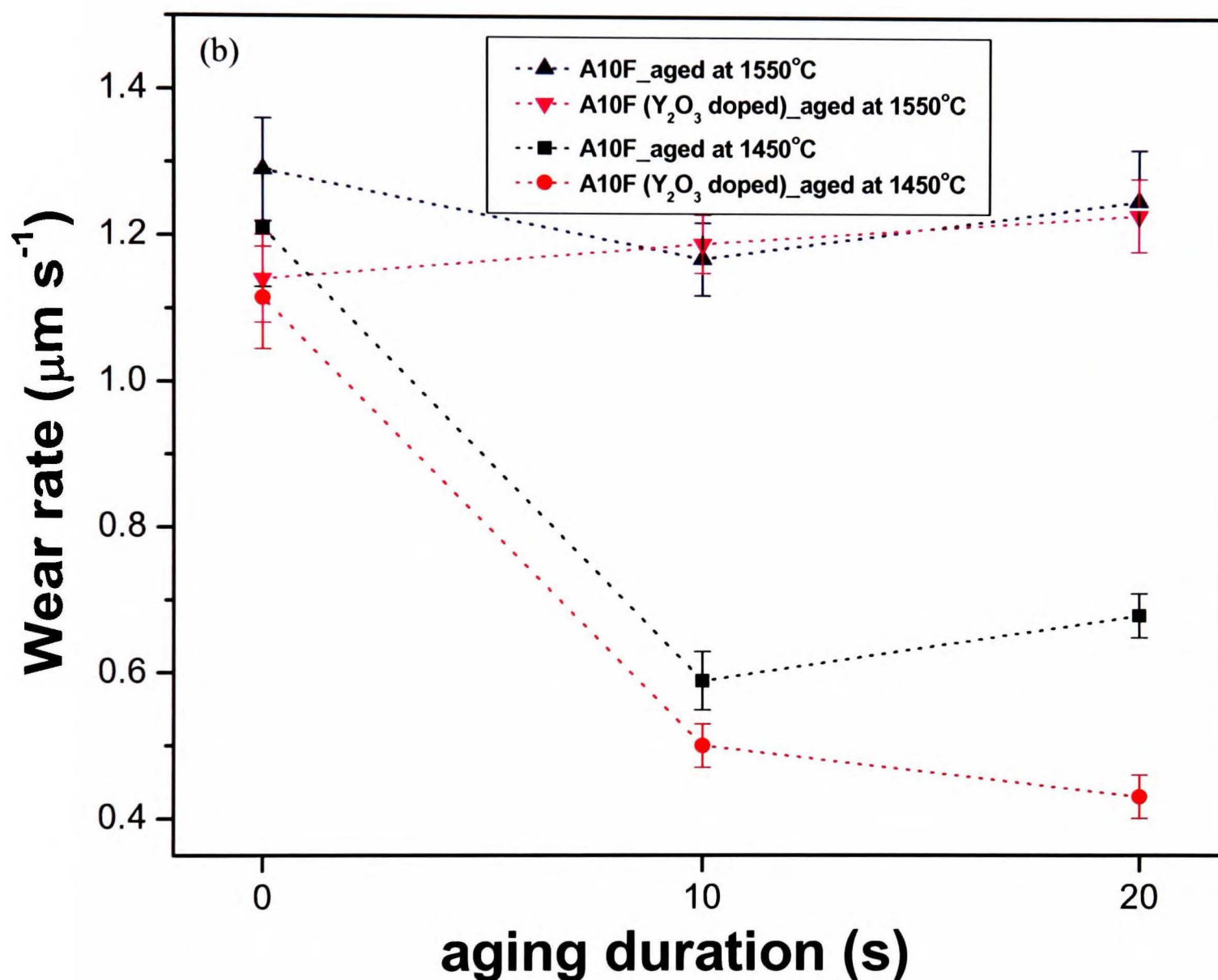


Fig. 5.1. (a) Plot of abrasive wear rates against aging duration for the Al_2O_3 - FeAl_2O_4 particulate nanocomposites developed on reduction aging at 1450°C . The wear rates measured for the monolithic alumina as well as the Al_2O_3 - 10 wt.% Fe_2O_3 solid solution are also presented for comparison. The effects of addition of ~ 250 ppm of Y_2O_3 on the corresponding wear rates are reported. (b) Plot of abrasive wear rates against aging duration at 1550°C for the Al_2O_3 - FeAl_2O_4 particulate nanocomposites (in the presence and absence of Y_2O_3 doping). The results for the nanocomposites developed at 1450°C are also presented for comparison.

5.1.2. Observation of the Worn Surfaces

In order to gain an insight into the wear mechanisms, topographical observations of the worn surfaces were made using SEM. The images corresponding to the worn surfaces of monolithic alumina, solid solution and the nanocomposites developed via reduction aging at 1450°C and 1550°C are presented in Figs. 5.2 to 5.5.

The worn surfaces of monolithic alumina shows the classical features of extensive pullout [1-9], whereby large pieces of material get removed by brittle fracture (Fig. 5.2a). The average pullout diameter has been estimated to be $\sim 4.5 \mu\text{m}$, which is larger than the Al_2O_3 grain size ($\sim 3 \mu\text{m}$). Such pullouts occupy an area fraction of $\sim 53\%$. Closer look into the pulled out regions reveals that such pullout formation occurred due to intergranular fracture (inset of Fig. 5.2a). Similar to that of alumina, the worn surfaces of A10F solid solutions can also be characterised by the presence of extensive intergranular fracture induced pullouts (Fig. 5.2a). Due to the extremely rough topography of the worn surfaces, with nearly $\sim 80\%$ of the area of the surfaces showing the presence of pullouts, precise estimation of the pullout size and area fraction occupied by pullouts could not be made.

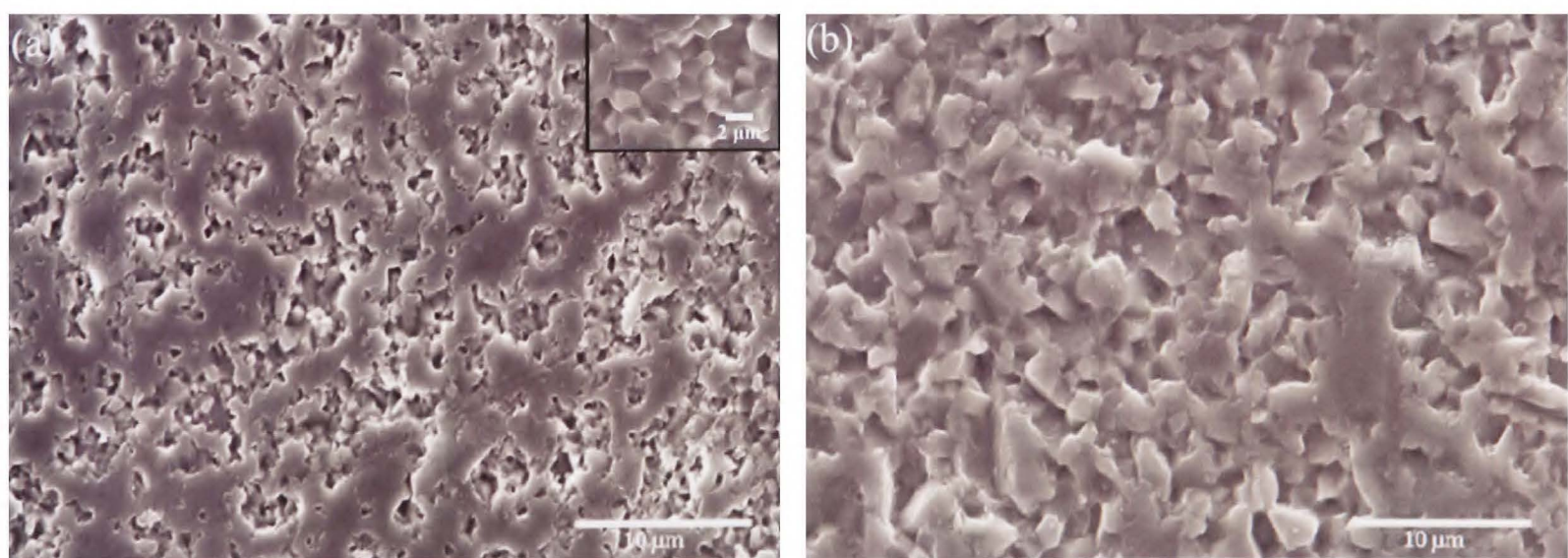


Fig. 5.2. SEM images of worn surfaces of (a) monolithic Al_2O_3 and (b) Al_2O_3 - 10 wt.% Fe_2O_3 (A10F) solid solution. Inset of (a) presents a higher magnification view of one of the pullouts.

Fig. 5.3 presents the worn surfaces of the nanocomposites developed on aging of A10F solid solutions (without yttria) at 1450°C. It can be observed that the composite developed on aging for 0 h (Fig. 5.3a) suffered intergranular fracture induced pullouts similar to those of monolithic Al₂O₃ (Fig. 5.2a) and A10F solid solution (Fig. 5.2b). By contrast, the worn surfaces of the nanocomposites developed on aging for 10 h (Fig. 5.3b) and 20 h (Fig. 5.3c) appear to be significantly different. Broadly, the nanocomposites developed after aging for 10 and 20 h tend to develop much smoother worn surfaces with much less extensive pullouts than was seen in the single phase materials. Furthermore, though suppressed with respect to monolithic alumina, careful observations do reveal the presence of abrasive scratches, along with some evidence of material removal by cutting and ploughing. Even though different in appearance from the conventionally observed pullouts in Al₂O₃ or Al₂O₃ - SiC nanocomposites [1-9], the presence of pullout like features can be observed on the worn surfaces (indicated by arrows) of these Al₂O₃ - FeAl₂O₄ nanocomposites. In fact, careful observation reveals that such pullouts can be grouped into two types. One set of pullouts have dimensions between 1 - 2 µm (some indicated by black arrows) and appear to have been formed due to some coarser intergranular second phase particles falling off during grinding, as can also be observed from the higher magnification image presented in Fig. 5.3d. The other set of pullouts, some of which are indicated with white arrows, are larger in dimensions (up to ~ 5 µm) and tend to be associated with transgranular fracture of the matrix grains (inset of Fig. 5.3c). Though precise estimation was not possible, it is quite apparent from the lower magnification images, as presented in Fig. 5.3b and c, that the pullouts due to transgranular fracture occurred less frequently and are much shallower as compared to the pullouts which appear to result from fall out of the intergranular second phase particles. Furthermore,

comparison of Fig. 5.3b and c also suggests that these later type of pullouts (indicated by black arrows) are more prevalent on the worn surface of the nanocomposite developed by aging for 20 h with respect to the nanocomposite developed after 10 h of reduction aging.

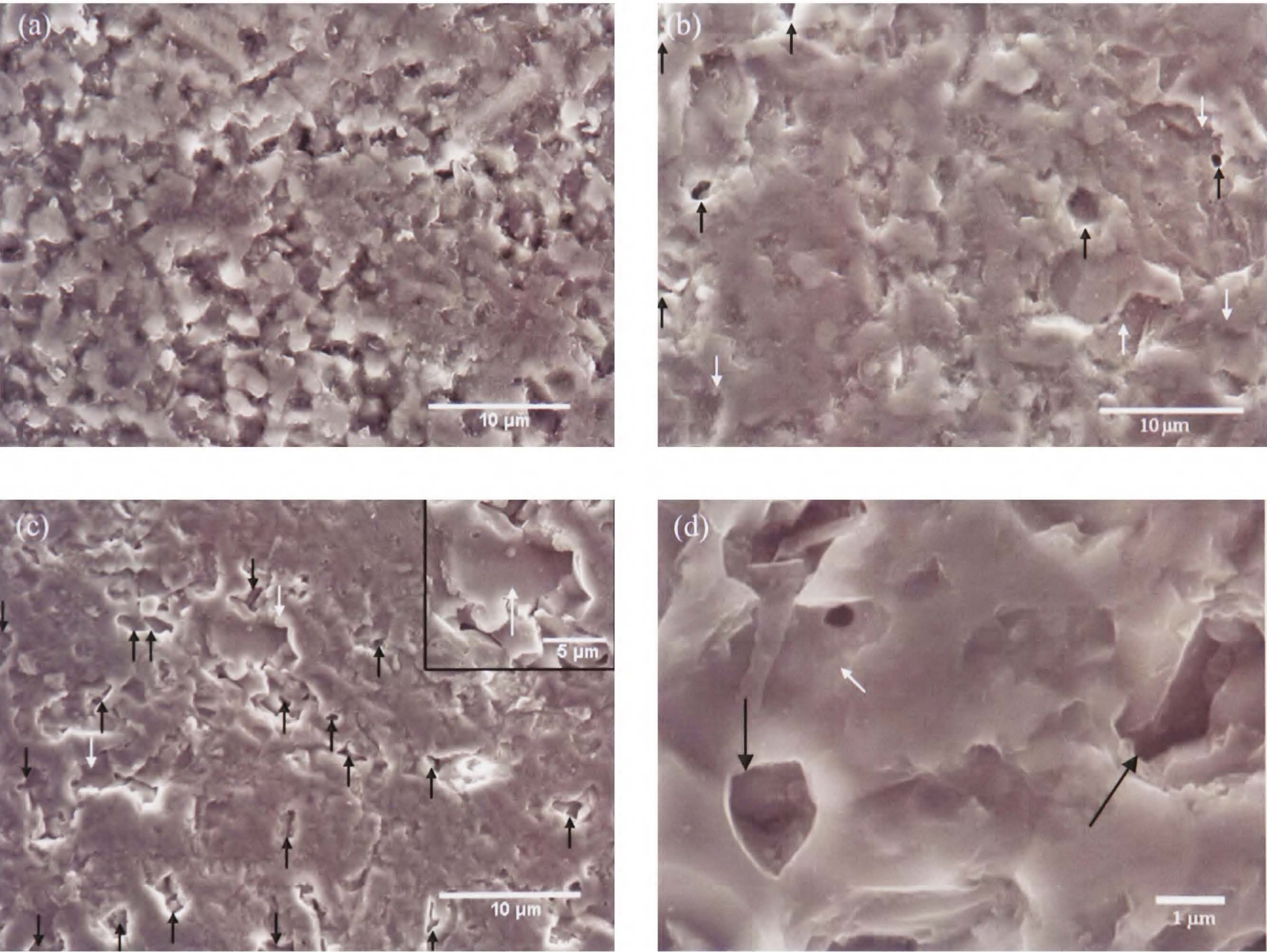


Fig. 5.3. SEM images obtained from the worn surfaces of the nanocomposites developed upon reduction aging of A10F at 1450°C for (a) 0 h; (b) 10 h; (c) and (d) 20 h. The black and white arrows indicate two different types of pullout like features. Inset of (c) presents a higher magnification view of one of the later types of pullouts.

The effect of Y_2O_3 doping on the appearance of the worn surfaces of the nanocomposites developed by reduction aging at 1450°C can be observed from Fig. 5.4. It can be observed that the features on the worn surfaces presented in Figs. 5.3a and 5.4a are quite similar, since intergranular fracture induced pullouts also occurred during the abrasive wear of the yttria-containing composite developed on aging for 0 h. By contrast, the worn surfaces of the yttria doped nanocomposites developed on aging for 10 h (Fig. 5.4b) and 20 h (Fig. 5.4b) appear to be almost completely devoid of any kinds of pullouts. Only abrasive scratches formed by plastic deformation can be observed on such worn surfaces. An interesting observation is the appearance of extremely fine particle like features of sizes varying between 100 - 300 nm throughout the worn surfaces of the Y_2O_3 containing nanocomposites developed after 10 and 20 h. From lower magnification images, as presented in Fig. 5.4a and b these features appear to be compacted wear debris. However, observations at higher magnification suggest that such features are inherent part of the structure of the worn surfaces (Fig. 5.4c). Such structures could correspond to new phase formed due to some tribochemical reactions. However no peaks, in addition to those present in the X-ray diffraction (XRD) patterns recorded with as polished surfaces of the nanocomposites, could be detected in the XRD patterns corresponding to the worn surfaces (Fig. 5.5a). By contrast, some broadening of the peaks corresponding to both the phases can be observed on closer look of the XRD patterns, which may be due to strain induced by plastic deformation (Fig. 5.5b). More detailed investigations are required to understand other plausible reasons behind the formation of such fine particle like features on the worn surfaces.

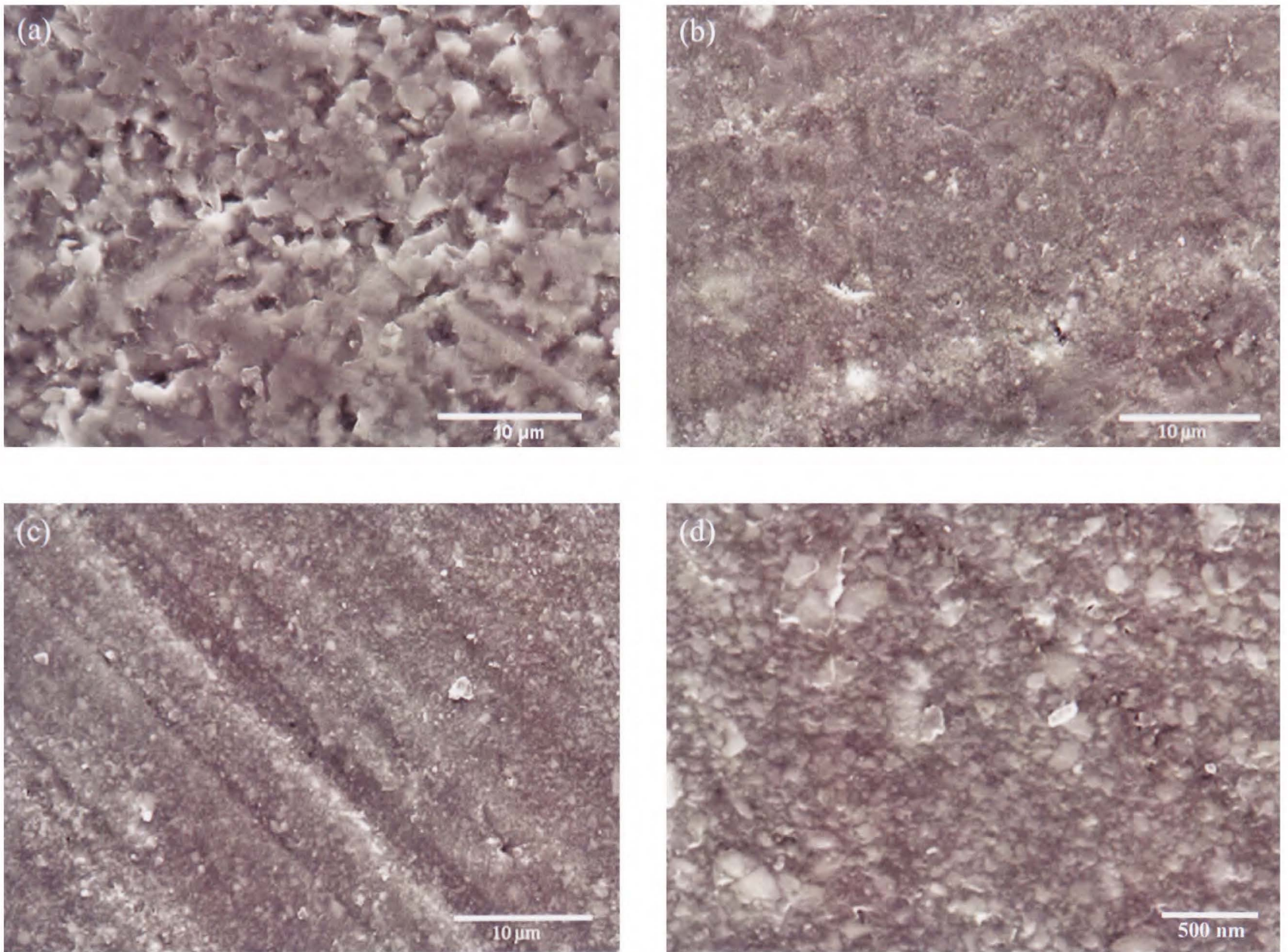


Fig. 5.4. SEM images obtained from the worn surfaces of the Y_2O_3 -doped nanocomposites developed upon reduction aging of A10FY at 1450°C for (a) 0 h; (b) 10 h; (c) and (d) 20 h. Note the almost complete absence of pullouts in (b) and (c).

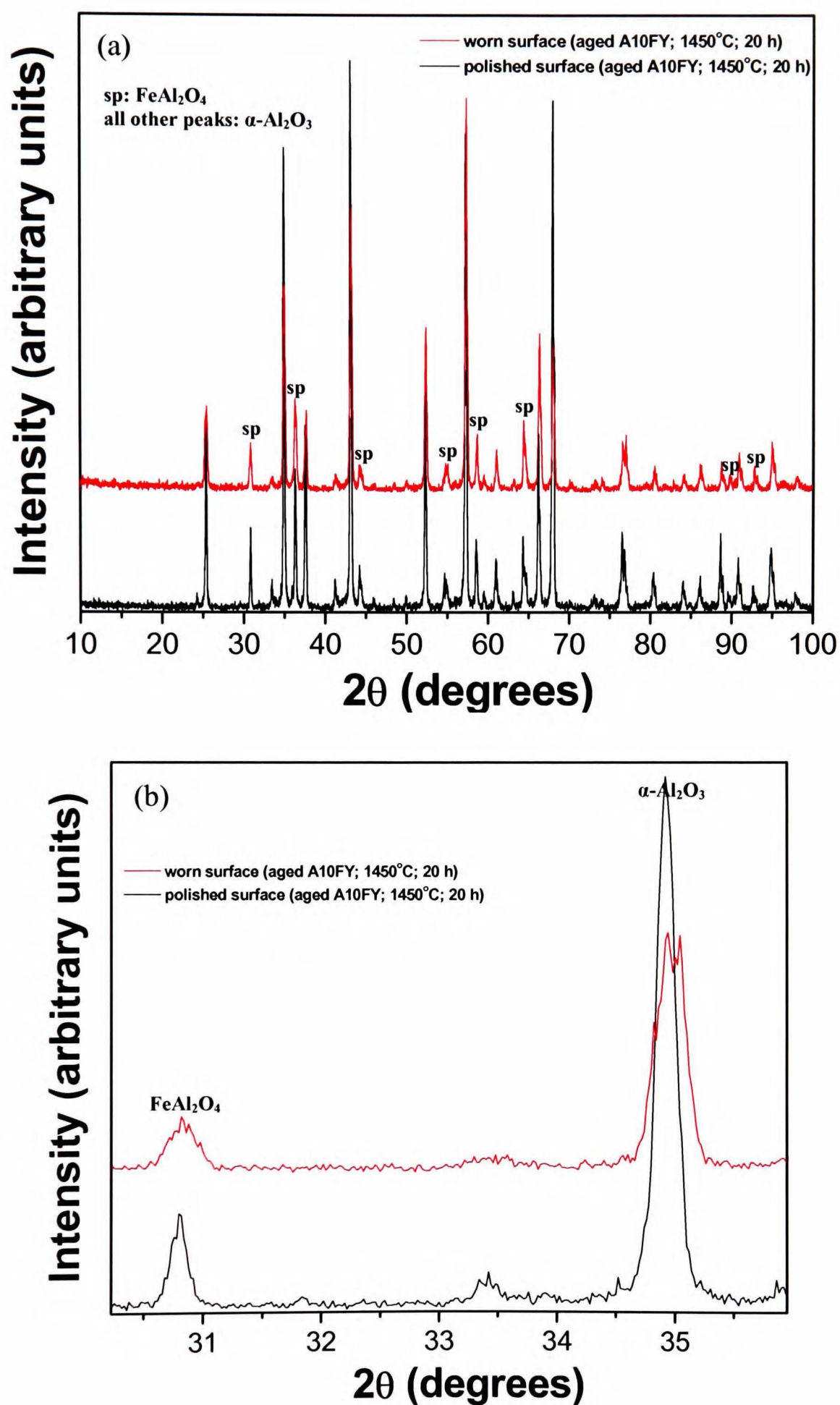


Fig. 5.5. (a) XRD patterns recorded from the polished and worn surfaces of nanocomposites developed by aging A10FY (~ 250 ppm Y_2O_3 -doped Al_2O_3 - 10 wt.% Fe_2O_3 solid solutions) at 1450°C for 20 h in reducing atmosphere ($\text{N}_2 + 4\% \text{H}_2$); (b) Magnified view of the FeAl_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ peaks indicating peak broadening in the pattern obtained from the worn surface.

SEM images of the worn surfaces obtained with the nanocomposites developed on aging at 1550°C are shown in Fig. 5.6. The composite not doped with yttria and developed at an aging duration of 0 h showed the presence of extensive pullouts caused by intergranular fracture (Fig. 5.6a). It may be recalled here that the composite developed at 1450°C for the same aging duration also presented worn surfaces characterized by the presence of such pullouts (see Fig. 5.3a). Though such pullouts due to intergranular fracture of matrix grains were suppressed on aging for longer durations, such nanocomposites suffered from extensive pullouts of the other two types, which are due to transgranular fracture of matrix grains and more significantly due to fall out of the coarser second phase particles (Fig. 5.6b). In contrast to the nanocomposites developed on aging at 1450°C, yttria doping did not have much effect on the appearance of the worn surfaces of the nanocomposites developed at 1550°C. To be precise, though intergranular fracture induced pullout seems to have been hindered for the nanocomposite developed for 0 h of aging, pullouts from falling out of the second phase particles occurred during the abrasive wear (Fig. 5.6c). Furthermore, the worn surfaces of the yttria containing nanocomposites developed after longer aging durations provide evidences for occurrence of extensive pullouts, both due to transgranular fracture and coarser second phase particles falling out (Fig. 5.6d).

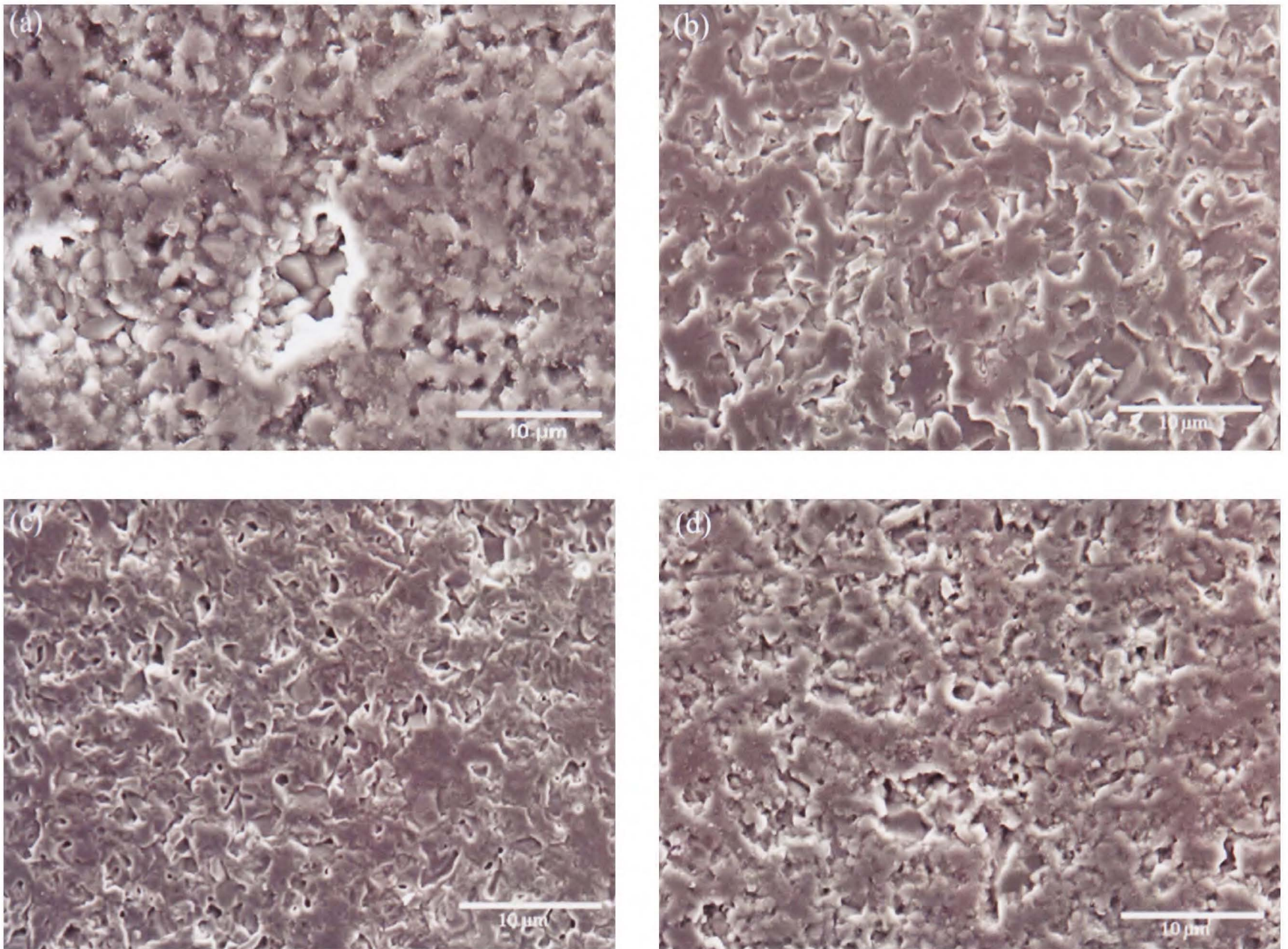


Fig. 5.6. SEM images obtained from the worn surfaces of the nanocomposites developed via reduction aging of A10F solid solutions at 1550°C for (a) 0 h; (b) 20 h; and reduction aging of A10FY (~ 250 ppm Y₂O₃-doped solid solutions) at 1550°C for (c) 0 h and (d) 20 h.

5.1.3. Indentation Polish Test

The ground and polished surfaces of monolithic Al_2O_3 , A10F solid solution and Al_2O_3 - FeAl_2O_4 nanocomposites were indented with Vickers indentation (load: 10 Kg). In order to investigate the subsurface damage caused by plastic deformation, the indented surfaces were further polished with 1 μm diamond paste and observed in SEM (see section 3.5 of chapter 3). The images of such indents after polishing (partly polished), along with those of the original indents before polishing are presented in Fig. 5.7. In the images of the partly polished indents (Fig. 5.7b, d and f), the remaining parts of the original indentations can be seen in the centre of the picture, along with the traces of the classical radial cracks outside the indentation plastic zone. The boundaries of the original indentations are indicated by dashed line. It is evident from Fig. 5.7b corresponding to monolithic alumina that whilst most of the surface has been well polished by the 1 μm diamond paste, a lot of pullouts due to intergranular fracture of the matrix grains occurred in a well-defined region corresponding closely to the shape and size of the indentation before surface removal by subsequent polishing. This is assumed to be the plastic zone beneath the indentation. Similar observations of the presence of extensive pullouts in the indentation plastic zone can be made from Fig. 5.7d, which correspond to the A10F solid solution. By contrast, the as polished indentation plastic zone corresponding to the nanocomposite developed upon aging at 1450°C for 20 h appears to be nearly devoid of any such pullouts (Fig. 5.7f). Such suppression of pullouts in the as polished indentation plastic zone, in contrast to that in monolithic Al_2O_3 , has been observed earlier also for Al_2O_3 - SiC nanocomposites [2].

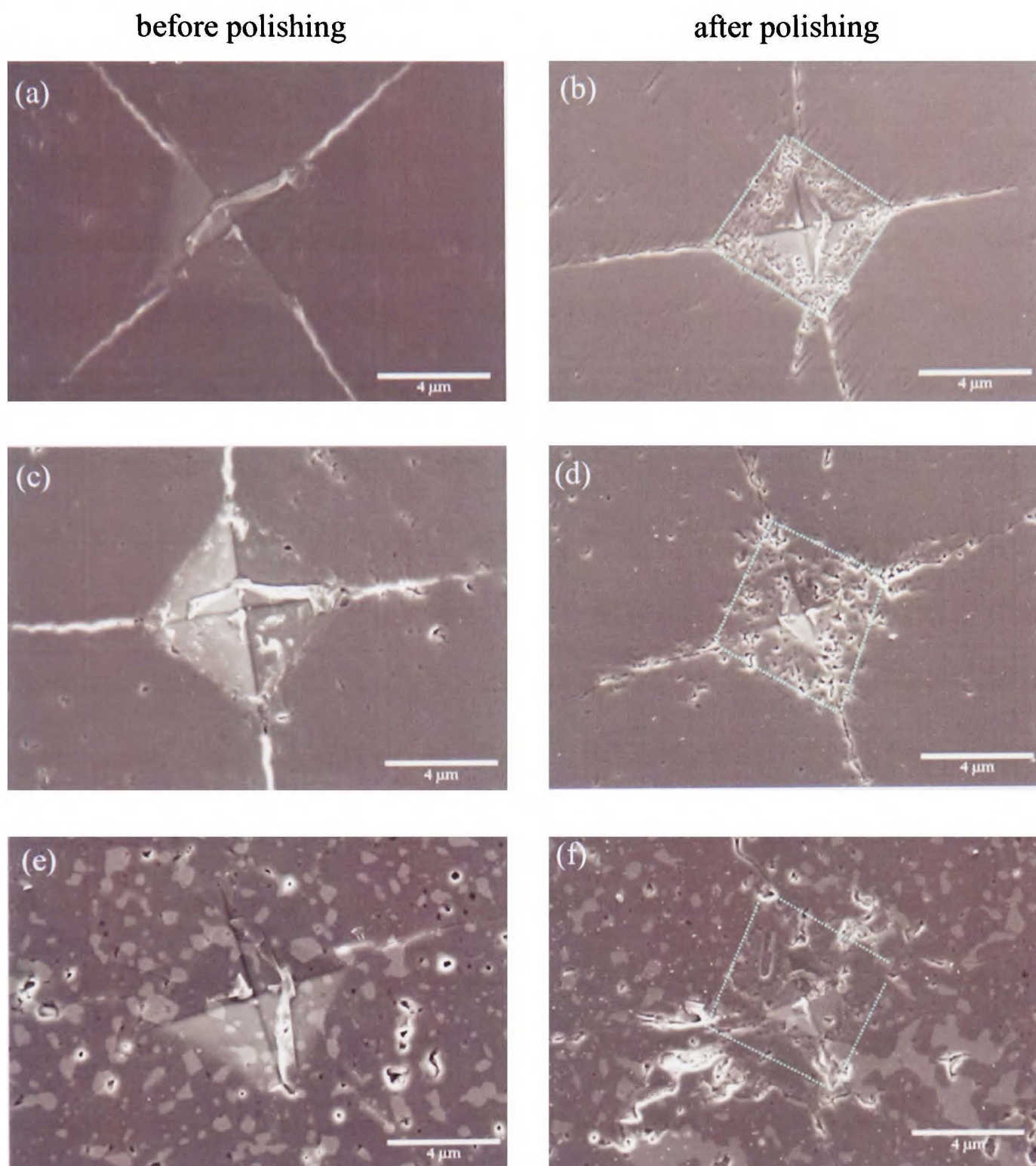


Fig. 5.7. SEM images of the original indentations (10 kg) and the partly polished remnant indentations (1 μm diamond paste), respectively, obtained on (a) and (b) monolithic Al_2O_3 ; (c) and (d) A10F solid solution; (e) and (f) nanocomposite developed on aging A10F for 20 h at 1450°C . Note the presence of extensive pullout induced cracking in the indentation plastic zones of the monolithic alumina and A10F solid solutions, but very little plasticity induced damage in the nanocomposites.

5.2. Discussion

5.2.1. Correlation between Microstructure Development, Fracture Mode and Appearance of Worn Surface

The results of the abrasive wear tests indicate that aging schedules, and concomitantly the microstructural developments, have significant influence over the wear behaviour of the Al_2O_3 - FeAl_2O_4 nanocomposites. It has been realised that, in general, reduction aging treatment for 0 h does not lead to any notable improvement in the wear resistance over that of monolithic Al_2O_3 or the Al_2O_3 - Fe_2O_3 solid solutions. On the contrary, wear resistance is improved with increase in aging time to 10 h at 1450°C . This is associated with the suppression of matrix grain pullouts induced by inter granular fracture (Figs. 5.2 to 5.4). It must be recalled here from the previous chapter that the nanocomposite developed on aging for 10 h at 1450°C exhibited a change in fracture mode from intergranular (for monolithic Al_2O_3 or A10F solid solution) to transgranular (see section 4.1.2.3 and Fig. 4.14). However, this change in fracture mode was not observed on reduction aging for 0 h. In this light, the suppression of pullouts for the nanocomposites can be correlated with the change in fracture mode to transgranular, which in turn gets correlated with the appearance of nanosized second phase particles on reduction aging for durations longer than 0 h at 1450°C (see chapter 4, section 4.1.1.2.2. and Fig. 4.6). Such analysis indicates that the presence of intragranular nanosized second phase particles is beneficial for the wear resistance of alumina, as opposed to the presence of coarser inter granular particles.

5.2.2. Role of Nanosized Intragranular Particles in Improving Wear Resistance

The results of the indentation polish test, as presented in section 5.1.3, provides an insight into the role of the intragranular nanosized particles towards suppressing intergranular fracture and concomitantly grain pullout during wear. It has been observed that polishing of the indents on monolithic alumina using 0.1 μm diamond paste leads to formation of pullouts in the as polished indentation plastic zone, whereas such pullout formation is suppressed in the nanocomposite developed on aging for 20 h at 1450°C. It must be noted here that the confinement of the pullouts produced in alumina only to the plastic zone of the indentation indicates that plastic deformation is responsible for the initiation of cracks that lead to pullout. Hence, the absence of such pullouts in the plastic zone of the nanocomposite is evidence of the ability of the nanosized second phase particles to suppress crack initiation during deformation. The absence of cracks or pullouts in the as polished surface outside the boundaries of the original indents confirms that though the mechanical polishing used was sufficiently gentle to avoid crack nucleation in undamaged areas, the polishing with 0.1 μm diamond paste was aggressive enough to propagate the incipient cracks in the plastic zone to result in the formation of pullouts in monolithic Al_2O_3 .

It has been reported earlier that room temperature compressive deformation [11], indentation [12], grinding [13] and abrasive wear [14] can result in the formation of deformation bands, mainly in the form of twins in Al_2O_3 . Furthermore, it has been observed that intersection of such twins and dislocation pile ups with the grain boundaries can result in the initiation of micro cracks and eventually grain boundary failure or intergranular fracture [11-15]. Guiberteau also observed that such grain boundary cracking due to intersection of the deformation bands occur mainly above a critical grain size [12]. In other words, as the grain size of monolithic alumina

increases, the lengths of the twins and the dislocation pile ups intersecting with the grain boundaries also increase, and above a critical size, the stress concentrations at the heads of such deformation bands evidently become sufficient to initiate grain boundary cracks in alumina [1,2]. In this perspective it is believed that presence of nanosized second phase particles within the matrix grains act as obstacles towards the formation of the twins and dislocations and concomitantly reduce their lengths and the stress concentration at their tips [1,2]. In fact, extensive interactions of the intragranular particles and dislocations/twins has been observed during TEM investigation of a thin foil prepared from the tensile region of one of the bent bars of the nanocomposites developed at 1450°C for 20 h (Fig. 5.8). Furthermore, in a similarly prepared TEM foil corresponding to monolithic Al₂O₃, the presence of numerous twins could be observed, most of which extend all across the grains from one grain boundary to the other (Fig. 5.8d). However, as can be observed from the higher magnification image (Fig. 5.8c) corresponding to the nanocomposite, the propagation of such twins was significantly suppressed in the presence of intragranular particles. It is quite apparent that some twins interacting with intragranular second phase particles got reduced in length and could not propagate through the matrix grain due to such obstructions. On a similar note, during an earlier TEM investigation of deformation structures beneath scratches and indentations by Wu and co workers [16,17], it was observed that long basal twins present in monolithic alumina were either absent or got reduced in penetration below the surface for the nanocomposites.

In more recent work, similar observations of suppression of pullout in the as polished indentation plastic zones were made for Al₂O₃ - SiC nanocomposites by Limpichaipanit and Todd [2]. In accordance with the earlier suggestion by Ortiz

Merino and Todd [1] it was hypothesized that cracking is suppressed due to intragranular SiC nanoparticles blocking the formation of long twins and dislocation pileups during plastic deformation in a mechanism similar to that of slip homogenisation in metals. Hence, in correlation with the literature reports pertaining to monolithic alumina and Al_2O_3 - SiC nanocomposites [1-14], the present observations suggest that there is a definite role of intragranular nanosized particles in preventing grain boundary fracture of matrix (Al_2O_3) grains. We believe that such phenomenon is also likely to have an influence on the change in fracture mode from intergranular to transgranular in the presence of intragranular nanosized particles.

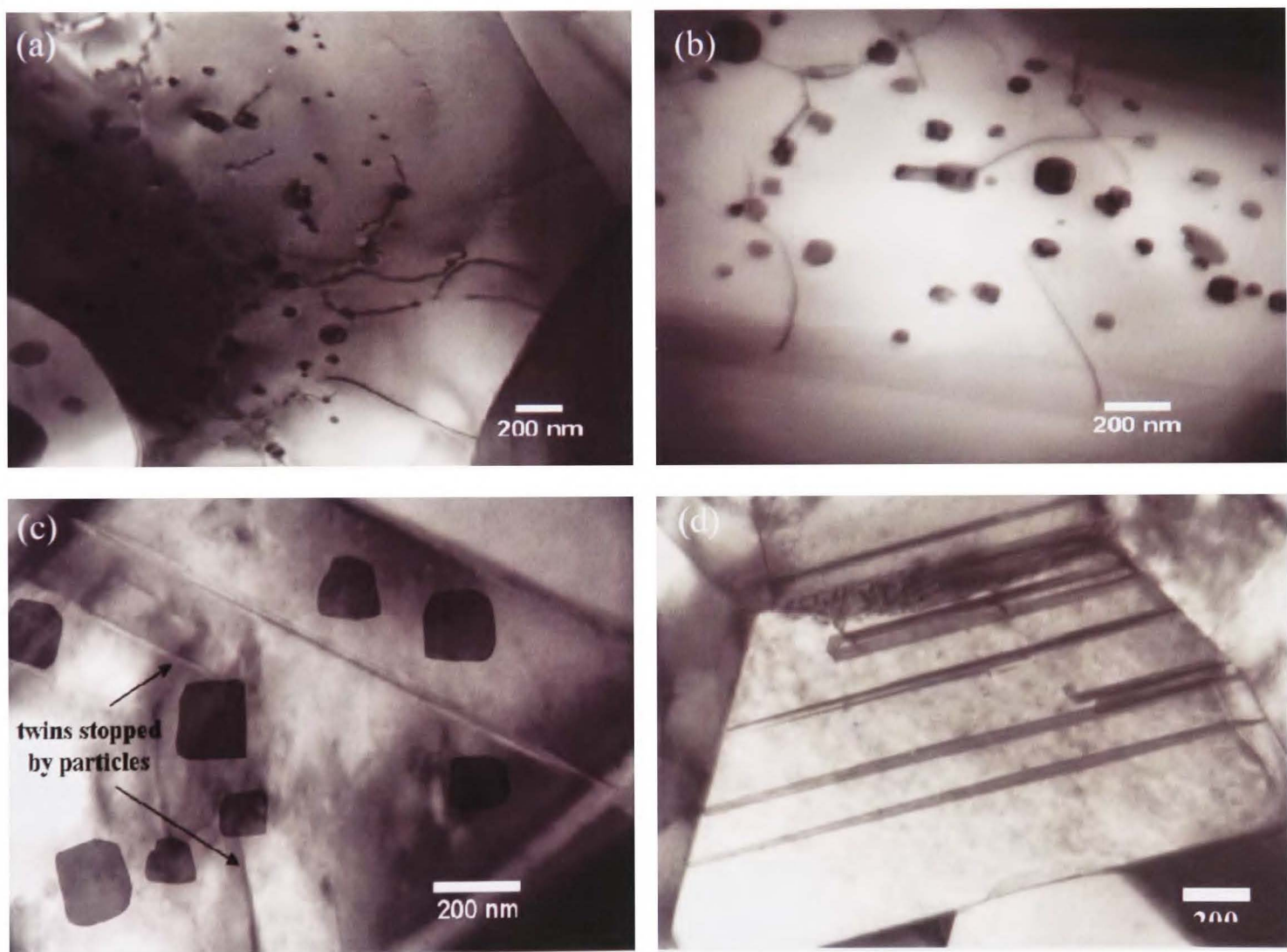


Fig. 5.8. Bright field TEM images showing (a,b,c) interaction of deformation bands (dislocations and twins) with intragranular nanosized particles in foil obtained from the tensile surface of bent bar of Al_2O_3 - FeAl_2O_4 nanocomposites, developed by reduction aging of A10F at 1450°C for 20 h; (d) twins propagating unhindered from one grain boundary to another in a foil obtained from the tensile surface of bent bar of monolithic Al_2O_3 .

5.2.3. Deleterious Effect of Coarser Intergranular Particles

The worn surfaces of the nanocomposites present evidence of pullouts occurring due to the falling out of the coarser, micron sized second phase particles, which were mostly present along the matrix grain boundaries (Fig. 5.3 and 5.6b to d). It has been further noted that the frequency of occurrence of such pullouts increased with the increase in aging duration, which in turn is correlated with the increase in average size of such intergranular second phase particles (see Table 4.1 and 4.2 of chapter 4). Additionally, the coarse intergranular particles, present in the nanocomposites developed after aging for 20 h, have also been observed to fall out during preparation of TEM samples (see Fig. 4.10d) and fracture during bend tests (see Fig. 4.14f). By contrast, the nanosized intragranular particles have rarely been observed to fall out in any of the processes.

Considering that the thermal expansion co-efficients of the matrix (Al_2O_3 ; $\alpha_m \sim 8 \times 10^{-6} \text{ K}^{-1}$ [18,19]) and the second phase particles (FeAl_2O_4 ; $\alpha_p \sim 13 \times 10^{-6} \text{ K}^{-1}$ [19]) are different, the contraction rates will be different for the two phases during cooling from the heat treatment temperatures. Due to this differential contraction rate, stresses develop within the phases and at the $\text{Al}_2\text{O}_3/\text{FeAl}_2\text{O}_4$ interfaces. Development of such stresses can effectively weaken the particle/matrix interfaces and even lead to spontaneous cracking at the interfaces, especially above a certain critical size of the second phase particles [20-23]. Furthermore, when the second phase particles, possessing higher thermal expansion co-efficients, contract more than the matrix during cooling, as in the present case, such spontaneous cracks are expected to develop circumferentially around the particles [20]. Neglecting the interaction between the second phase particles, the pressure (P) which the particles are subjected

to during cooling from the heat treatment temperatures can be approximately estimated from the following expression developed by Weyl [24] and Selsing [25];

$$P = \Delta\alpha\Delta T / [(1 + \nu_m) / 2E_m + (1 - 2\nu_p) / E_p] \quad (5.1)$$

In this equation, $\Delta\alpha = \alpha_m - \alpha_p \sim -5 \times 10^{-6} \text{ K}^{-1}$, ΔT is the cooling range over which plasticity is considered to be negligible $\sim 1000^\circ\text{C}$, ν_m and E_m are the Poisson's ratio (~ 0.2) and elastic modulus ($\sim 350 \text{ GPa}$) of the matrix (Al_2O_3) [26], ν_p and E_p are the Poisson's ratio (~ 0.3) and elastic modulus ($\sim 225 \text{ GPa}$) of the second phase particles (FeAl_2O_4) [27,28]. The above equation (5.1) gives a value of -1.4 GPa for the pressure (P) which the particles are subjected to.

Based on an energy balance criterion, Davidge and Green [20] developed the following expression for the critical radius of the second phase particles (R_c), above which spontaneous cracking is possible due to the pressure (P) developed during cooling from the fabrication/heat treatment temperature;

$$R_c = 8\gamma_s / [P^2 \{(1 + \nu_m) / E_m + 2(1 - 2\nu_p) / E_p\}] \quad (5.2)$$

Assuming γ_s as 2 J/m^2 for the interfaces of the Al_2O_3 matrix grain boundaries [29,30] with FeAl_2O_4 , a value of $1.1 \text{ }\mu\text{m}$ can be obtained for R_c . Hence such estimation indicates that second phase particles of sizes greater than $\sim 2 \text{ }\mu\text{m}$ are likely to develop spontaneous cracks along their interfaces with the matrix.

Broadly such analysis reveals that while the intragranular nanosized particles should be free from any cracking along the interface, the coarser micron sized intergranular secondary phase particles are more prone towards spontaneous cracking during cooling from the aging temperature. In fact, presence of micro cracks along the interface of such intergranular particles has been observed during TEM investigations (Fig. 5.9). Furthermore, since the stiffness of the second phase particles is different from that of the matrix, the particle/matrix interfaces of the coarser particles are more

vulnerable towards cracking due to stress magnification in the vicinity of the particles during application of external stresses [20,31-33]. To be more precise, the above analysis gives insight into the occurrence of extensive pullouts due to the intergranular particles falling out during wear of the nanocomposites, causing the wear rate to increase with increase in aging time from 10 h at 1450°C. It can be observed from Fig. 4.6 and Table 4.1, that as opposed to the nanocomposites developed after 10 h of aging, the average size of the intergranular second phase particles in the nanocomposites developed on aging for 20 h exceeds the critical size of $\sim 2 \mu\text{m}$ predicted based on the expression developed by Davidge and Green [20]. Hence, more particles are likely to fall out during wear of the latter nanocomposite due to failure at the cracked interfaces. Hence, the presence of such coarser intergranular particles, especially above a certain size of $\sim 2 \mu\text{m}$ as is present in the Al_2O_3 - FeAl_2O_4 nanocomposites developed by aging for durations greater than 10 h at 1450°C (see Table 4.1), is deleterious for the wear resistance. It can be further observed that with yttria doping, the average size of the intergranular particles, even after aging for 20 h, gets reduced to $\sim 1.2 \mu\text{m}$ (see Table 4.2), which is below the critical limit. It is quite likely that such effect of the presence of Y_2O_3 on the particle sizes leads to reduction in pullout of the intergranular particles and concomitantly the measured wear rate. Furthermore, it can be observed that in all the nanocomposites developed at 1550°C the average sizes of the intergranular particles are greater than the critical size, irrespective of the absence or presence of yttria (see Table 4.1 and 4.2). Hence, such nanocomposites exhibit inferior wear resistance, even in the presence of yttria. On a different note, the considerably lower hardness of the nanocomposites developed at the higher aging temperature of at 1550°C (see Table 4.3) might also contribute towards deteriorating the wear resistance.

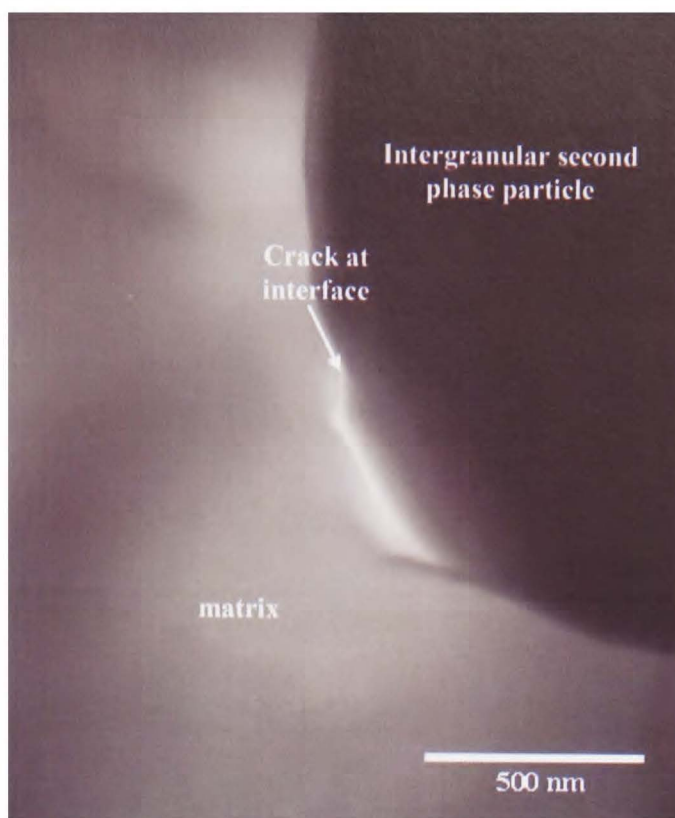


Fig. 5.9. Bright field TEM micrograph showing the presence of crack at the interface of the intergranular particle with the matrix.

5.3. Summary and Outlook

The Al_2O_3 - FeAl_2O_4 nanocomposites developed at the optimum aging conditions possess improved abrasive wear resistance (comparable to Al_2O_3 - SiC nanocomposites), accompanied by suppression of brittle intergranular fracture induced grain pull outs, with respect to monolithic alumina. Presence of yttria (~ 250 ppm) doping further improved the wear resistance of the nanocomposites by suppressing the formation of coarse intergranular particles. The ability to yield structures with a doubling of commercially important properties such as wear resistance by cheaper processing route, as described in the present work, is undoubtedly of great commercial significance.

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Chapter 6

MICROSTRUCTURE DEVELOPMENT AND MECHANICAL PROPERTIES OF ABS - MWCNT NANOCOMPOSITES

The feasibility of developing dense nanocomposites of aluminoborosilicate (ABS) glass-ceramic reinforced with well dispersed multiwalled carbon nanotubes (MWCNTs), up to MWCNT contents of 15 wt.%, has been investigated. The processing is done using a recently developed sol-gel based processing route [1]. The dispersions achieved with different amounts of MWCNT reinforcements have been reported. The mechanical properties of the ABS - MWCNT nanocomposites are analysed with respect to the reinforcing mechanisms of carbon nanotubes, and in correlation with the MWCNT contents.

6.1. Results

6.1.1. Densification, Phase Evolution and Microstructural Development

The sintered densities (as % of the theoretical densities; ρ_{th}) of the hot pressed ABS glass and ABS - MWCNT nanocomposites are reported in Table 6.1. The densities of both the glass and the MWCNT were assumed to be 2.2 gm/cm³ [2]. While unreinforced ABS glass could be densified to near theoretical density ($\sim 100\% \rho_{th}$), slightly lower densities ($\sim 96 - 98 \% \rho_{th}$) were measured with the nanocomposites. This is consistent with earlier observations that carbon nanotubes inhibit densification when added to glass-ceramic materials [2-5]. However, the present densities are considerably higher than those obtained in previous attempts to develop nanocomposites of borosilicate glass reinforced with 10 wt.% MWCNT via hot pressing [2,5]. Hence, this processing route allows the attainment of good sintered densities ($> 95 \% \rho_{th}$) for higher nanotube contents (~ 15 wt.%) at modest hot pressing temperatures (below 1000°C), which is also beneficial in terms of avoiding damage to the carbon nanotubes [1,6].

Table 6.1. Sintered densities of the hot pressed unreinforced ABS glass-ceramic and ABS - MWCNT nanocomposites, as determined via Archimedes’ method.

materials	sintered densities (% ρ_{th})
unreinforced ABS	99.8
ABS - 2.5 wt.% MWCNT	98.2
ABS - 5 wt.% MWCNT	97.9
ABS - 10 wt.% MWCNT	97.5
ABS - 15 wt.% MWCNT	96.1

XRD spectra, as obtained with hot pressed conventional borosilicate glass (BSG; containing 5 wt.% Al_2O_3) - 5 wt.% MWCNT nanocomposite, unreinforced ABS glass-ceramic (with higher Al_2O_3 content ~ 22 wt.%) and ABS - (5 - 15 wt.%) MWCNT nanocomposites, are presented in Fig. 6.1. The presence of peaks corresponding to cristobalite can be observed in the nanocomposite developed using BSG. It has been reported that the presence of cristobalite in BSG is detrimental since it leads to matrix cracking and concomitant degradation of properties, due to volume changes accompanying its displacive transformation during cooling from hot pressing/sintering temperatures [1,4,7]. On the contrary, following our previous work [1], addition of excess Al_2O_3 (up to ~ 22 wt.%) during sol-gel processing (of ABS glass), resulted in complete suppression of cristobalite formation. Instead, the addition

of this excess Al_2O_3 (up to ~ 22 wt.%) resulted in the formation of crystalline Mullite, which can be detected in the XRD patterns corresponding to unreinforced ABS as well as the ABS - MWCNT nanocomposites. The particle sizes of mullite crystallites, as estimated via the Scherrer equation using the full widths at half-maxima of the diffraction peaks corresponding to (120), (001), (111) and (002), vary between 17 - 22 nm for all the compositions. The extent of the crystallization, as judged by the relative heights of the peaks in Fig. 6.1, appears similar in all the materials.

In accordance with the results of density measurements, the absence of residual porosity can be noted from SEM images of the polished surfaces of hot pressed unreinforced ABS and ABS - MWCNT nanocomposites (Fig. 6.2). The polished surfaces present a smooth appearance and are devoid of any cracks. This further confirms that addition of excess (~ 22 wt.%) Al_2O_3 and the concomitant suppression of the formation of cristobalite prevented cracking during cooling from the hot pressing temperature. This result is in agreement with the observations made in the previous report [1].

An important observation is that the as polished surfaces appear to be virtually featureless for pure glass as well as the nanocomposites containing MWCNT up to 10 wt.% (Fig. 6.2a,b). This suggests that the nanotubes were well dispersed at contents up to 10 wt.%. However, features resembling pull-outs occurring during grinding/polishing of polycrystalline ceramics are prevalent on the polished surfaces of the ABS - 15 wt.% MWCNT nanocomposite (Fig. 6.2c). It is believed that such features correspond to carbon nanotube agglomerates.

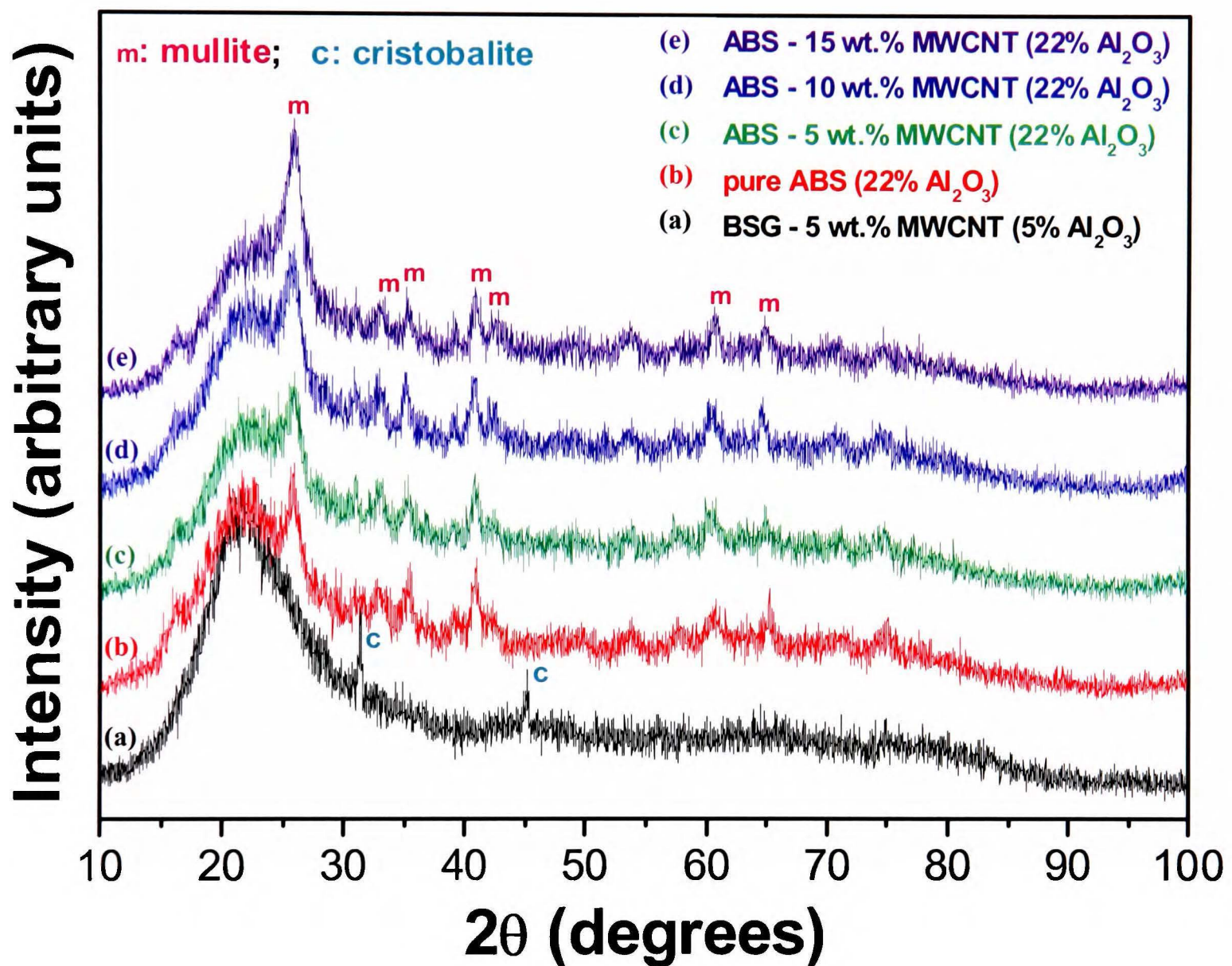


Fig. 6.1. X-ray diffraction (XRD) spectra obtained with hot pressed (a) conventional borosilicate glass (BSG; containing only ~ 5 wt.% Al_2O_3) reinforced with 5 wt.% MWCNT showing the presence of cristobalite (c); (b) pure aluminoborosilicate glass (ABS; containing higher Al_2O_3 content ~ 22 wt.%); (c) ABS - 5 wt.% MWCNT nanocomposite; (d) ABS - 10 wt.% MWCNT nanocomposite; (e) ABS - 15 wt.% MWCNT nanocomposite, showing the presence of mullite (m), instead of cristobalite.

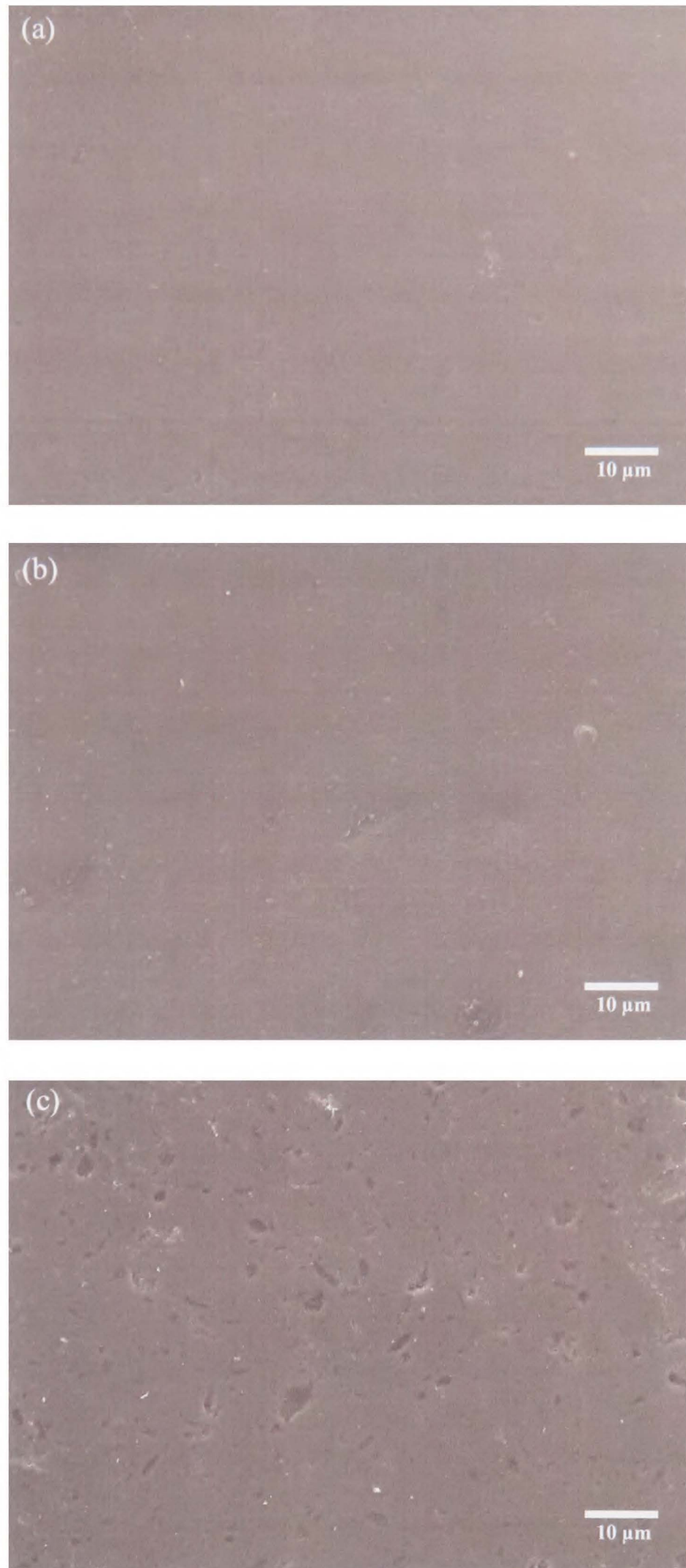
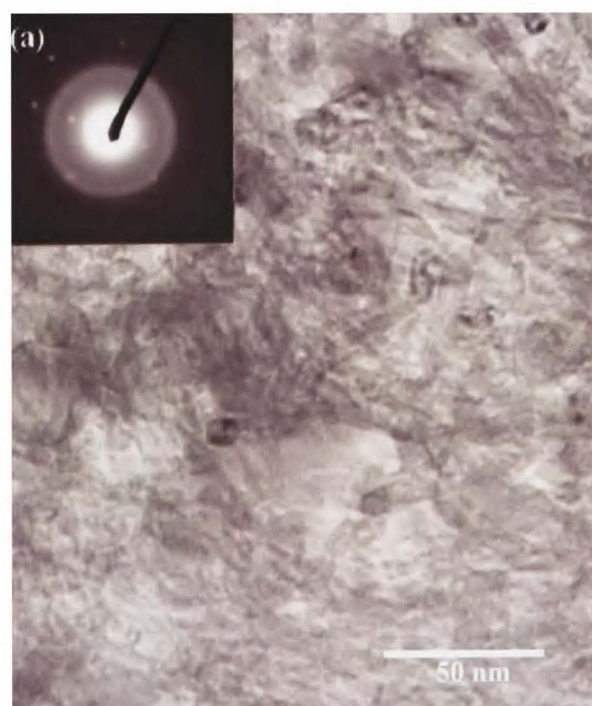
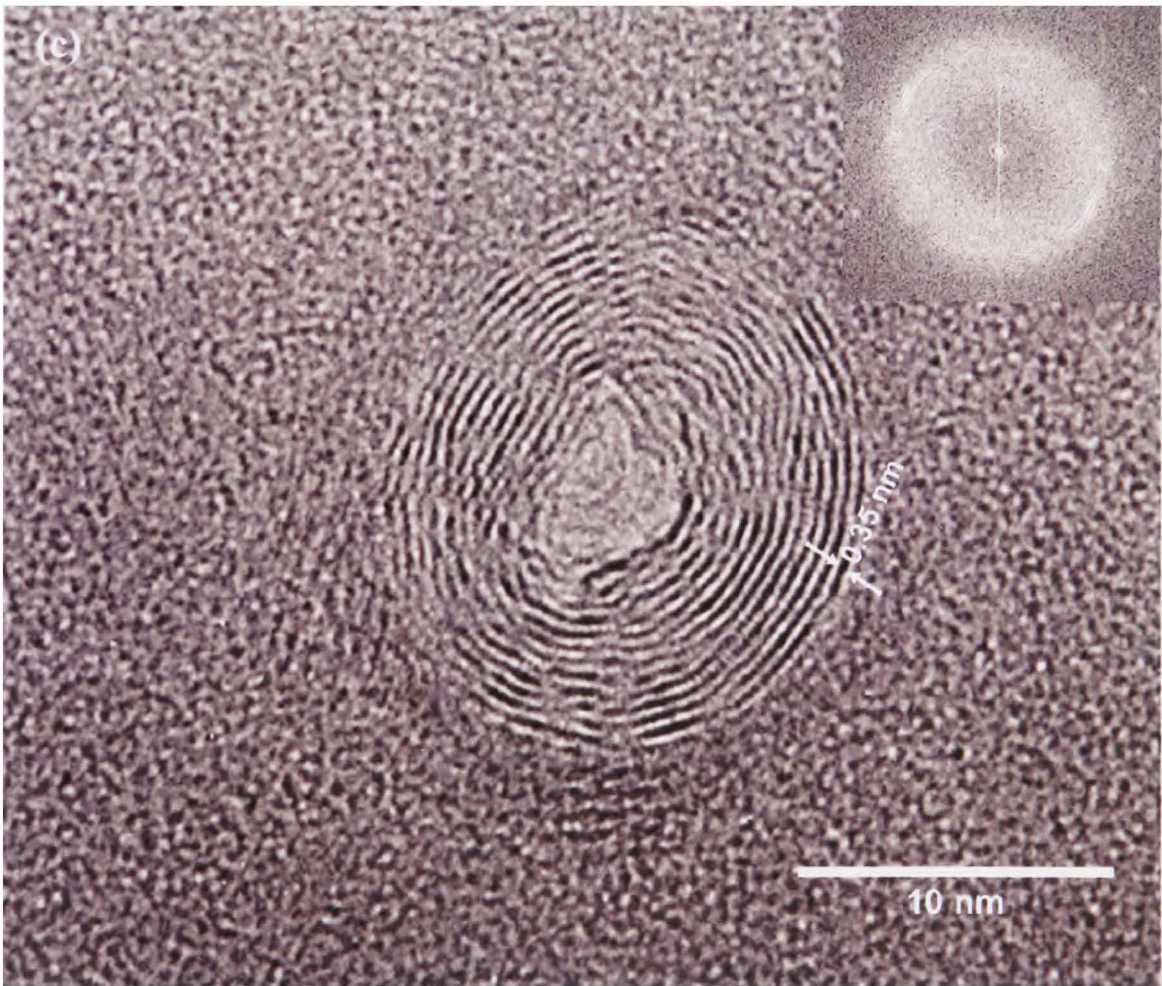
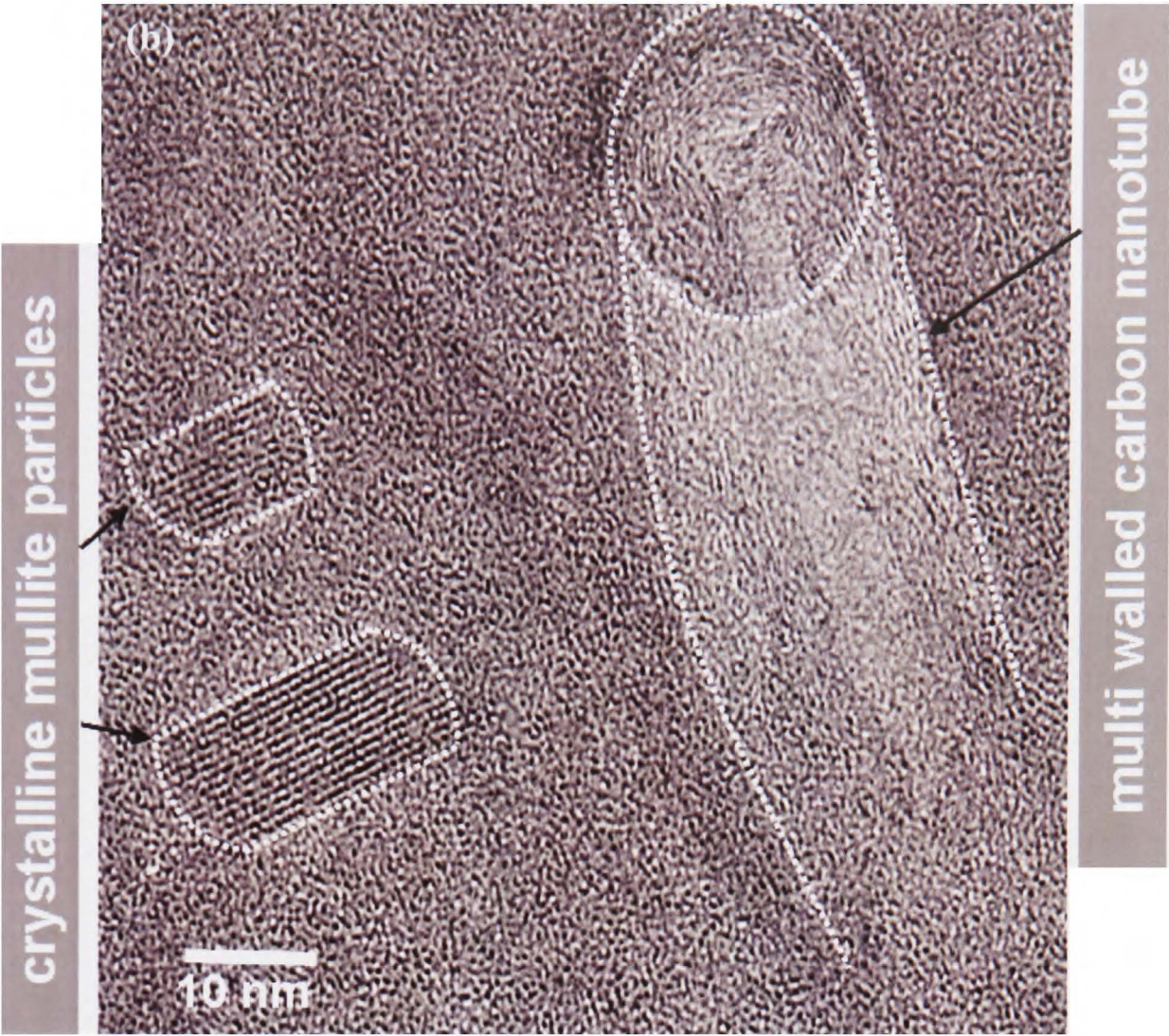


Fig. 6.2. SEM micrographs of as polished surfaces of (a) monolithic ABS glass-ceramic; (b) ABS - 10 wt.% MWCNT nanocomposite and (c) ABS - 15 wt.% MWCNT nanocomposite.

A network of carbon nanotubes can be observed on lower magnification TEM images obtained with hot pressed ABS - 10 wt.% MWCNT nanocomposite (Fig. 6.3a). Spots seen in the diffraction pattern (inset of Fig. 6.3a) obtained from a wide area reveal the presence of crystalline phase in the glass - CNT composite. High resolution TEM images (Fig. 6.3b,c) of the nanocomposites confirmed the presence of multi-walled carbon nanotubes, demonstrating that they had survived the processing and heat treatment. The numbers of walls have been found to vary between 11 and 15, with an inter-wall spacing of around 0.35 nm, which is very close to the typical inter-sheet spacing of graphite [8]. In the previous work [1], the presence of undamaged MWCNTs in such nanocomposites has also been confirmed using Raman spectroscopy. Along with the presence of MWCNTs, crystalline particles having sizes varying between 10 - 20 nm can also be observed throughout the microstructure (Fig. 6.3b and d). In one such crystalline particle, as presented in Fig. 6.3d, spacings between two clear lattice fringes have been measured by image analysis software to be ~ 0.75 nm and 0.76 nm, which are consistent with the (100) and (010) planes, respectively, of orthorhombic mullite ($d_{100} \sim 0.76$ nm; $d_{010} \sim 0.78$ nm as in Card No: 84-1205 of JCPDS-ICDD). Such fringes are oriented at an angle of 90° to each other, as is consistent with the crystal structure of Mullite.





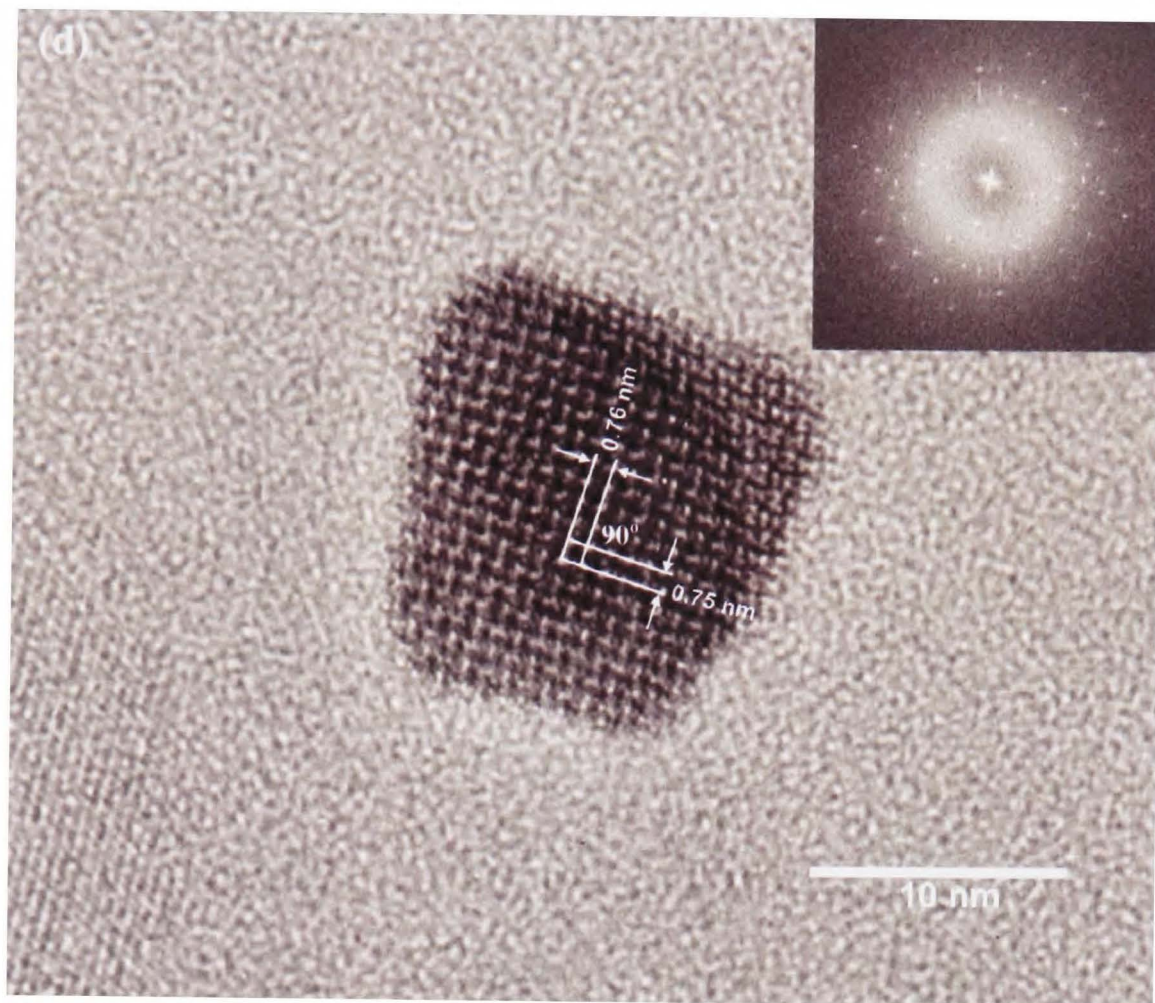


Fig. 6.3. (a) Low magnification TEM image showing a network of carbon nanotubes in ABS - 10 wt.% MWCNT nanocomposite. Diffraction spots corresponding to crystalline phase can be seen in the SADP (inset); (b) High resolution TEM micrograph confirming the presence of MWCNT, along with the crystalline particles; (c) closer look, along with Fast Fourier Transform (FFT), at one of the MWCNTs showing an inter wall spacing of ~ 0.35 nm and (d) closer look, along with Fast Fourier Transform (FFT), at one of the crystalline particles showing clear lattice fringes having an angle of 90° between them and having spacings of ~ 0.75 nm and ~ 0.76 nm.

6.1.2. Hardness and Elastic Modulus via Indentation

Hardly any cracking could be observed around the Berkovich nanoindentations (maximum load: 140 mN) obtained on the unreinforced ABS and the ABS - MWCNT nanocomposites (Fig. 6.4a). However, the macro Vickers indentations (maximum load: 2 kg) suffered from extensive cracking (Fig. 6.4b,c), which made it difficult to accurately measure the hardness using such indentations. SEM images of the residual Vickers indentations, obtained at a load of 2 kg, reveal the presence of extensive ring cracks as well as lateral cracking, especially for the monolithic ABS glass-ceramic (Fig. 6.4b,c). Such ring cracking is typical of the anomalous glasses like borosilicate glass, which tend to densify under the indentation load [9,10]. However, the important observation is that the lateral cracking, which is so severe in Fig. 6.4b that a large chip has been removed around the indentation, is almost totally suppressed for the ABS - MWCNT nanocomposites (Fig. 6.4c). This indicates that the presence of carbon nanotubes leads to improved damage tolerance under contact loading for the nanocomposites, as compared to the unreinforced glass-ceramic. Such improvements in tolerance of surface damage have also been reported earlier for CNT reinforced polycrystalline ceramics [11,12].

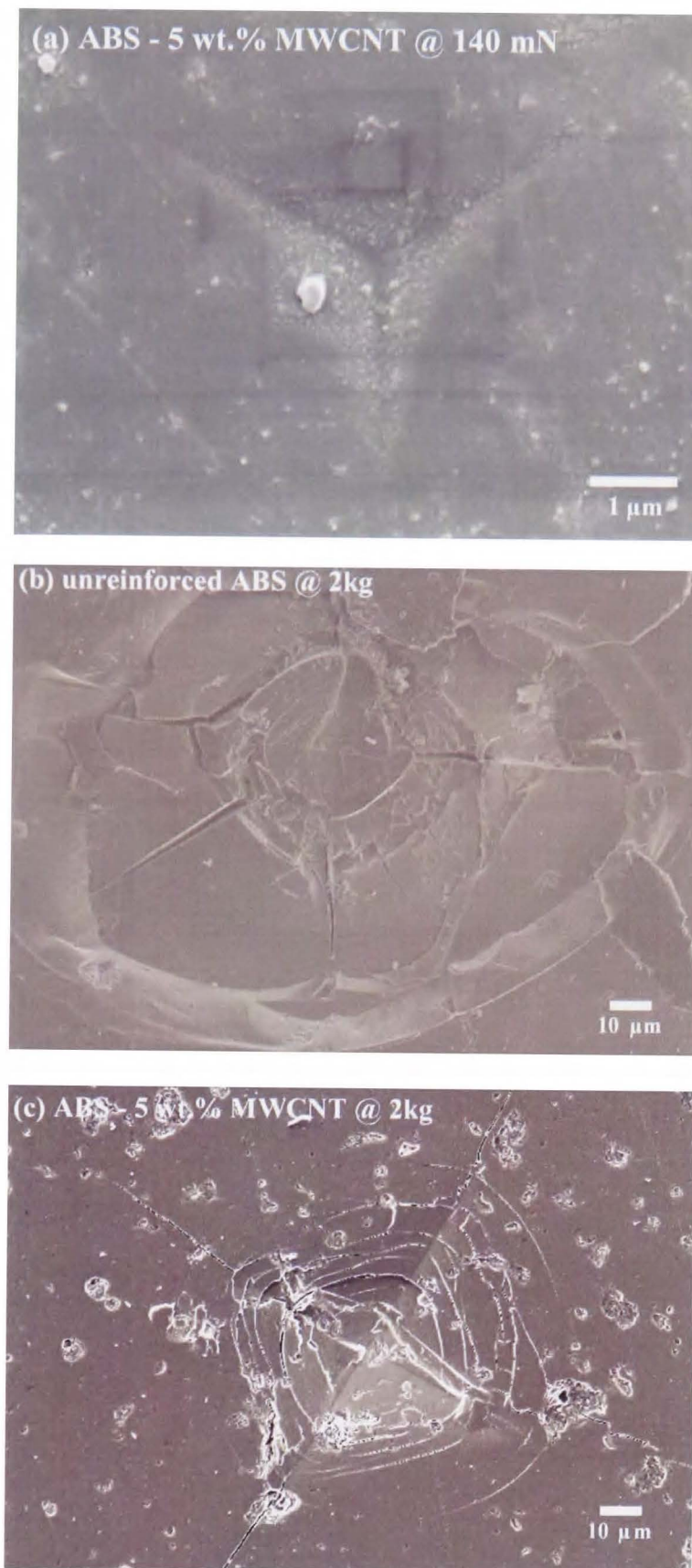


Fig. 6.4. SEM images of indentations obtained on (a) ABS - 5 wt.% MWCNT using Berkovich nano indenter at a maximum load of 140 mN; (b) unreinforced ABS glass-ceramic and (c) ABS - 5 wt.% MWCNT using Vickers indentation at a load of 2 Kg. Note that while ring cracking, typically observed during indentation of anomalous glasses such as borosilicate glass is present in both (b) and (c), the presence of carbon nanotubes considerably suppress the lateral cracking around the Vickers indentation on the nanocomposite (c).

The hardness results obtained with the nano-indentations are reported in Table 6.2. Incorporation of MWCNTs in the ABS glass-ceramic led to a modest reduction in hardness. The slightly lower sintered densities of the MWCNT containing ABS glass-ceramics may be partly responsible for this lowering of hardness. Such reductions in hardness on the incorporation of carbon nanotubes in inorganic matrices have also been observed by others [3,5,12,13].

Table 6.2. Hardness and Elastic Modulus, as measured via Berkovich nano indentation, for the hot pressed unreinforced ABS glass-ceramic and ABS - MWCNT nanocomposites.

materials	hardness (nano indentation; GPa)	Elastic Modulus (nano indentation; GPa)
unreinforced ABS	10.4 ± 0.4	81.3 ± 2.7
ABS - 2.5 wt.% MWCNT	8.1 ± 0.5	64.8 ± 3.8
ABS - 5 wt.% MWCNT	8.8 ± 0.7	76.4 ± 4
ABS - 10 wt.% MWCNT	9.0 ± 0.3	78.1 ± 3.3
ABS - 15 wt.% MWCNT	7.2 ± 0.9	71.9 ± 5.9

Fig. 6.5 and Table 6.2 present the elastic modulus (*E*) results as a function of MWCNT content. After an initial drop in elastic modulus with the incorporation of a small amount (2.5 wt.%) of MWCNT, the modulus rose with further increases in MWCNT content up to 10 wt.%, which suggests that some load transfer from the matrix to the CNTs is possible during the application of stress, albeit a small amount. However, the elastic modulus dropped with further increase in the MWCNT content

up to 15 wt.% and this may be explained by the agglomeration of the MWCNTs (see Fig. 6.2c). None of the nanocomposites was as stiff as the unreinforced ABS.

Fig. 6.5 also presents a conservative rule of mixtures estimate of the composite elastic modulus. This estimate considers that only $1/3^{\text{rd}}$ of the volume fraction of the nanotubes are aligned along the stress direction to bear any load, while the remaining $2/3^{\text{rd}}$ simply act as pores, which are assumed to lower the elastic modulus by twice their volume fraction [14]. For the rule of mixtures estimation, a modest value of 500 GPa was assumed for E of the functionalized CVD grown multiwalled nanotubes used in the present work. Xie et al. [15], as well as Pan et al. [16], obtained similar values for E during stress-strain measurements of CVD grown MWCNT bundles and such relatively modest values have been attributed to the defects present on the MWCNT [1,15,16]. The lower values of the experimentally determined elastic moduli for the nanocomposites, as compared to even such a conservative estimate, imply that the effective bonding between the ABS matrix and the MWCNT is weak, resulting in ineffective load transfer.

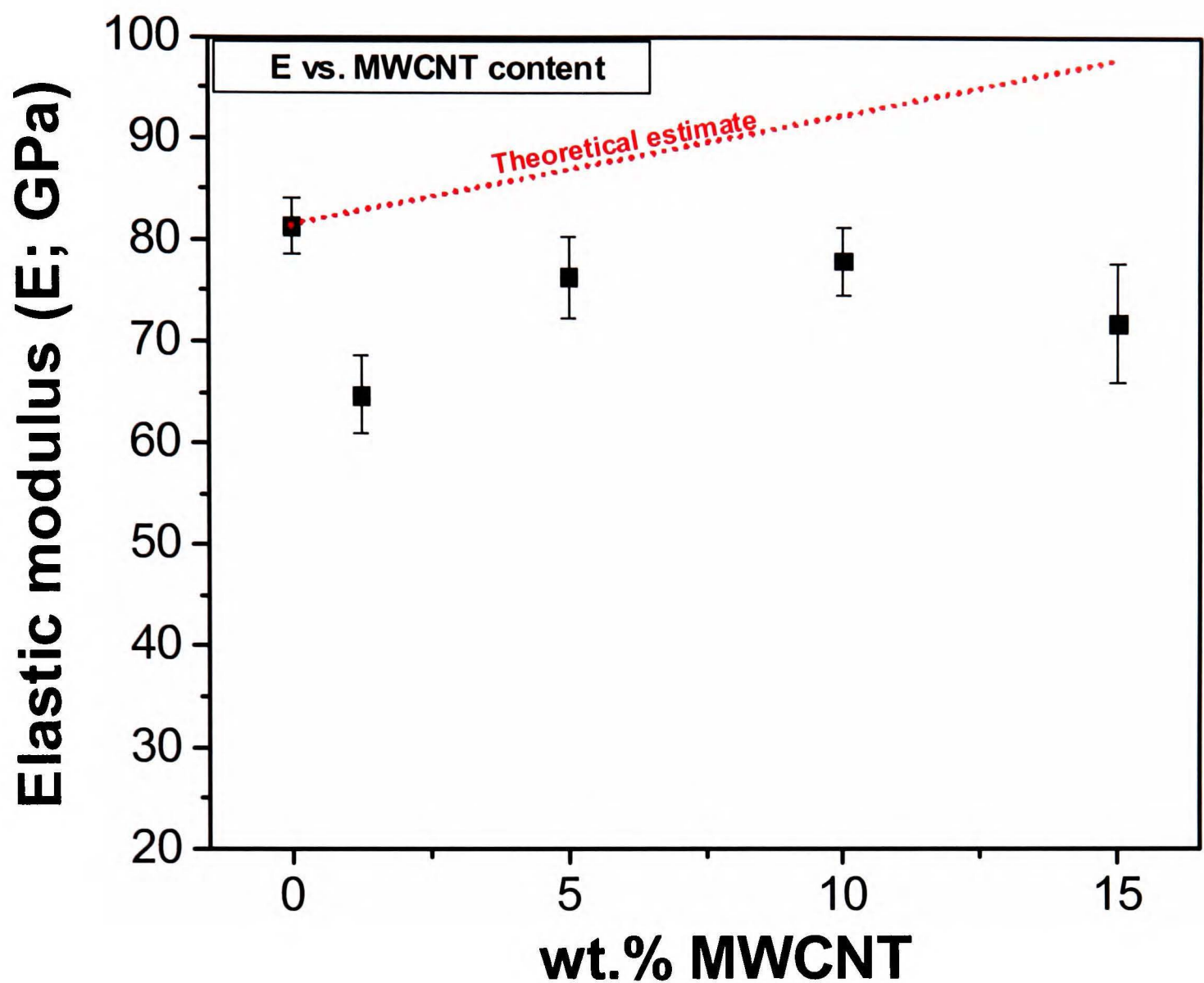


Fig. 6.5. Variation of elastic modulus (E) with MWCNT content. It can be noted that the experimentally measured stiffness fall below the most conservative theoretical estimate using rule of mixtures for randomly oriented fibre reinforced composites (dotted line).

6.1.3. Flexural Strength and Fracture Toughness

The variation of fracture toughness with MWCNT content is presented in Fig. 6.6a. The fracture toughness improved markedly with the incorporation of MWCNTs, reaching a maximum of $\sim 1.6 \text{ MPa m}^{1/2}$ at 10 wt.% MWCNT content, as compared to only $\sim 0.7 \text{ MPa m}^{1/2}$ for unreinforced ABS glass. Such a significant improvement in fracture toughness, by as much as $\sim 150\%$ over that of the unreinforced glass-ceramic

matrix, has not been reported previously. Furthermore, the present results support the very few earlier reports [4,17,18] claiming that the cheaper and more easily available MWCNTs (as compared to SWCNTs) can indeed be used as reinforcing fibres to toughen and strengthen brittle inorganic matrices.

The flexural strengths of the unreinforced ABS glass-ceramic and the ABS - MWCNT nanocomposites are presented in Fig. 6.6b. The flexural strength increases steeply with the MWCNT content and is nearly doubled with the incorporation of 10 wt.% MWCNT. The excellent dispersion of the MWCNTs, so that large flaws are not formed with up to 10 wt.% MWCNTs (Fig. 6.2b), is believed to be one of the factors responsible for enabling this large improvement in fracture toughness, also to be reflected in the strengths of the nanocomposites. The literature survey reveals that improvement of flexure strength to such an extent has not been possible in earlier research efforts concerned with the reinforcement of borosilicate glass with carbon nanotubes [5]. Furthermore, in more conventional fibre reinforced or ceramic platelet reinforced borosilicate glass matrix composites, improvements of only a maximum of ~ 60% in strength could be achieved with 5-12 vol.% NextelTM fibres [19] and ~ 20% with Al₂O₃ platelets [20], as against nearly 100% improvement for the present ABS - 10 wt.% MWCNT nanocomposites. In fact with respect to both the flexural strength and the fracture toughness, the present results show the biggest improvements reported in the literature pertaining to CNT reinforced inorganic glassy matrices [4,5,17], in cases where it is clear that the improvements are due directly to the CNTs and not to indirect effects on the microstructure. However, a further increase in MWCNT content up to 15 wt.% resulted in a considerable lowering of the strength. This is assumed to be a consequence of the inability to homogeneously disperse the

nanotubes at or above 15 wt.% leading to the creation of large defects due to MWCNT agglomeration (see Fig. 6.2c).

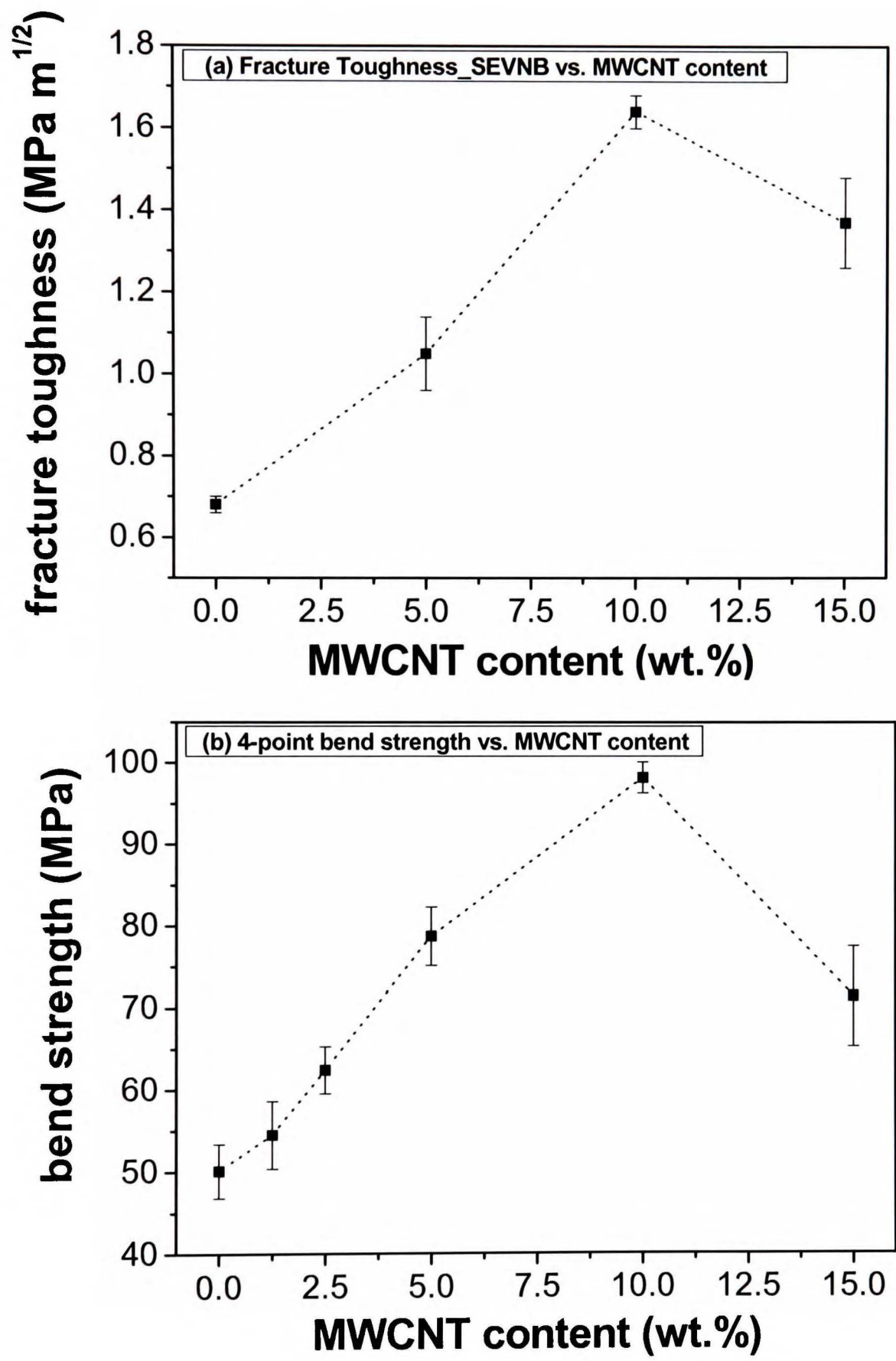


Fig. 6. Variation of (a) fracture toughness (SEVNB) and (b) flexural strength (4-point bending) with MWCNT content. The fracture toughness, as well as the bend strength, gets significantly improved with respect to unreinforced ABS glass-ceramic with incorporation of carbon nanotubes upto ~ 10 wt.%.

6.1.4. Observations of Fractured Surfaces and Crack - MWCNT Interactions

SEM micrographs of fractured surfaces of the nanocomposites, generated during fracture toughness testing (SEVNB), are presented in Fig. 6.7. In accordance with the densification results (Table 6.1) and the images obtained from the polished surfaces (Fig. 6.2), hardly any residual porosity can be observed. Also, the fractured surfaces further confirm the absence of CNT agglomeration in the nanocomposites containing up to 10 wt.% MWCNT. However, regions of agglomerated MWCNTs can be seen on the fractured surfaces of the composites containing the highest investigated amount (15 wt.%) of nanotubes. Nevertheless, the ability of the present processing route to disperse at least 10 wt.% of MWCNTs represents a considerable advancement over previous reports [2,5].

An important observation that can be made from the fractured surfaces is the absence of any holes left by pulled out nanotubes. Holes are expected to be left on the fractured surface if nanotubes were pulled out from their matrix socket during separation of the crack faces. Additionally, SEM images obtained with the fractured surfaces at near glancing angles to the incident electron beam (Fig. 6.8a) show that essentially all the protruding sections of the nanotubes are of 50 nm or less in length. The absence of pull-out induced holes is also supported by AFM observation of fractured surfaces (Fig. 6.8b,c). The three dimensional view of the AFM image of fractured surfaces confirms that the nanotubes protrude from the fractured surfaces by lengths less than ~ 50 nm (Fig. 6.8c).

Another interesting observation that can be made from the fractured surfaces is that the protruding MWCNTs have diameters that appear considerably larger than the diameters of the as functionalised MWCNTs. High magnification images clearly reveal that the apparent diameters of the MWCNTs on the fractured surfaces of the

hot pressed nanocomposites are around 40 nm (Fig. 6.9), as compared to ~ 25 nm or less for the as functionalised MWCNTs [1]. Fig. 3a,b confirms that the nanotubes in the composites retain their original diameters and are not swollen by intercalation. Furthermore, the surfaces of the protruding nanotubes appear rough which, along with the above observations, suggests that glass from the matrix adheres strongly to the surface of the MWCNT. This implies that debonding takes place away from the actual interface and within the matrix. Such observations also show that the ‘sword-in-sheath’ type of failure, which is typical of MWCNTs in other conditions [21], did not occur here. ‘Sword-in-sheath’ type of failures usually occur when the outer walls of the nanotubes bear most of the load and fail, while the inner walls remain intact and tend to get ‘telescoped’ out due to the weak inter-wall bonding of MWCNTs. Such a failure mode would have resulted in the protruding MWCNTs having diameters smaller than the diameter of the as functionalised MWCNTs, which is contrary to our observations.

Additionally, we note that the SEM micrograph in Fig. 6.9 shows no evidence of the axial hole down the centres of the nanotubes. Inspection of the existing literature base reveals that the axial CNT holes are generally not seen on SEM images of fractured surfaces. The TEM images in Fig. 6.3a and b makes clear that a central region free of graphene layers is in fact present in the nanocomposites on such images [2,4,22,23]. We believe that the apparent absence of this region in SEM micrographs is a result of an electron optical artefact associated with secondary electron imaging.

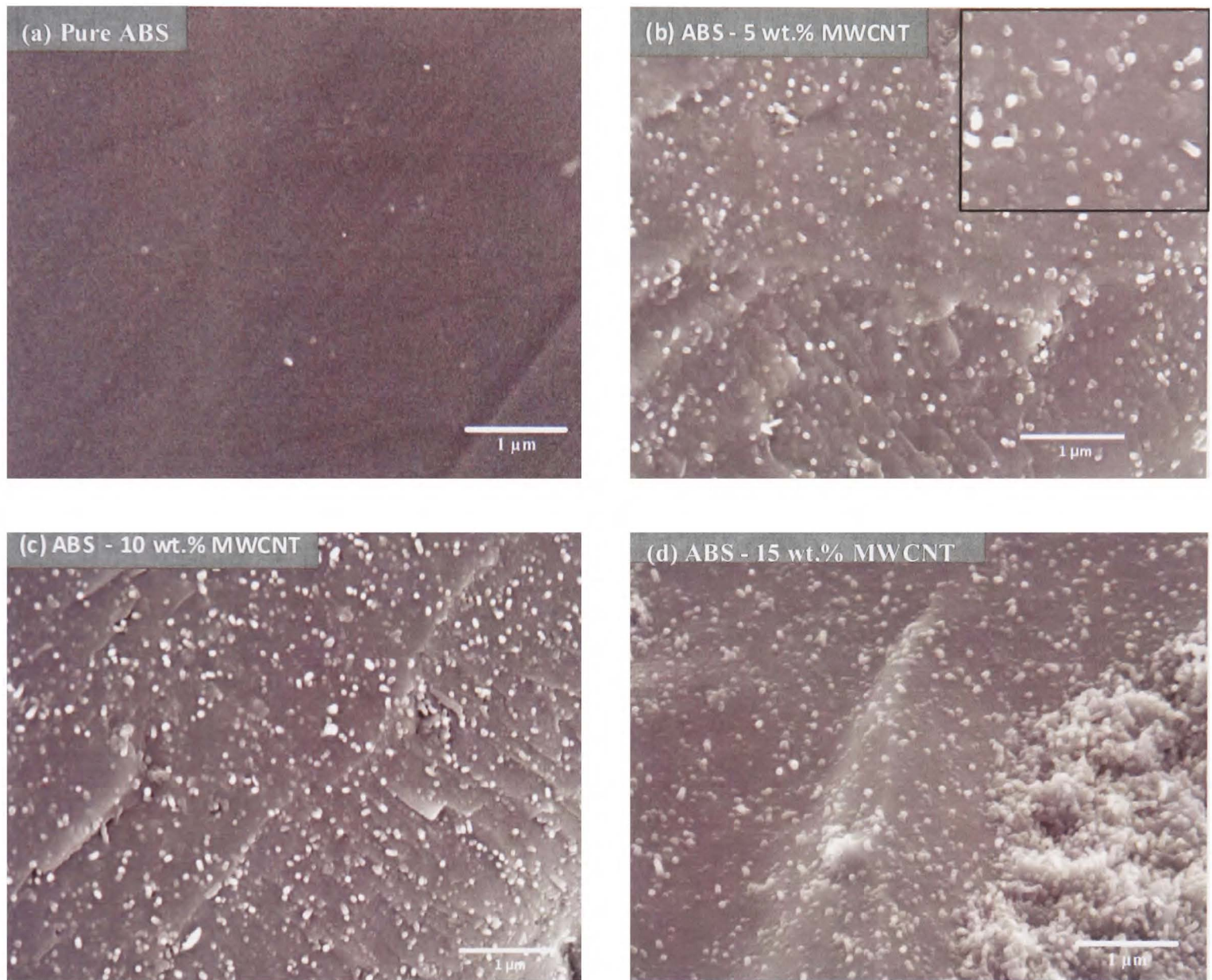


Fig. 6.7. SEM micrographs of fractured surfaces obtained during bend tests for (a) unreinforced ABS glass-ceramic; (b) ABS - 5 wt.% MWCNT; (c) ABS - 10 wt.% MWCNT and (d) ABS - 15 wt.% MWCNT. Note that carbon nanotubes are homogeneously dispersed in the nanocomposite containing upto 10 wt.% MWCNT (b and c). However, agglomeration of the nanotubes occur on increasing the content to 15 wt.% (d).

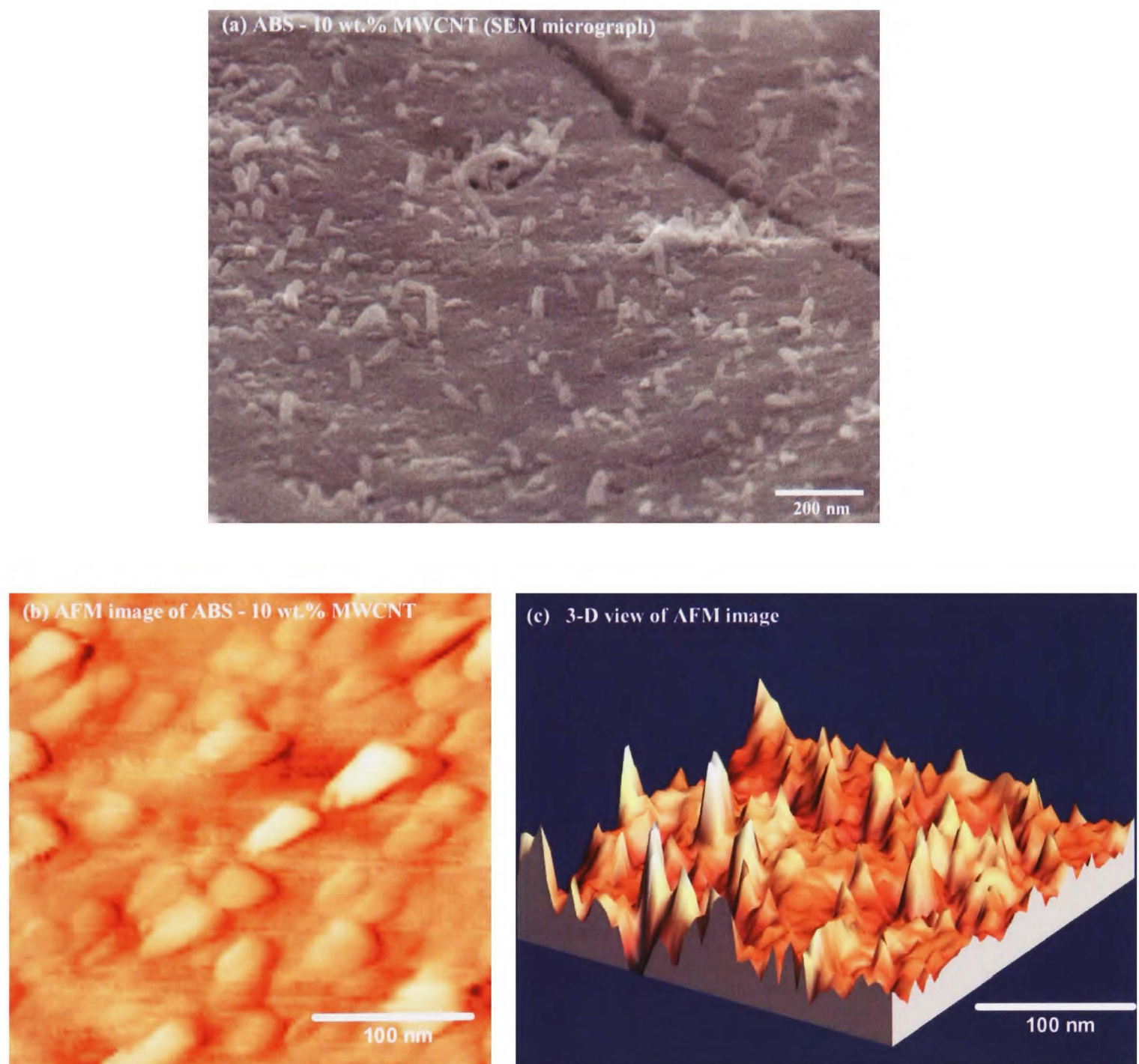


Fig. 6.8. Fractured surfaces of ABS - 10 wt.% MWCNT as observed in (a) SEM, with fractured surface at near glancing angle with incident electron beam and (b) AFM; (c) 3 dimensional view of the AFM image. It can be noted that the nanotubes protrude the fractured surface by very small lengths of around 50 nm and random variations in protruding lengths generated due to fibre (MWCNT) pull-out can not be observed. The absence of any holes (pull-out induced) is further confirmed.

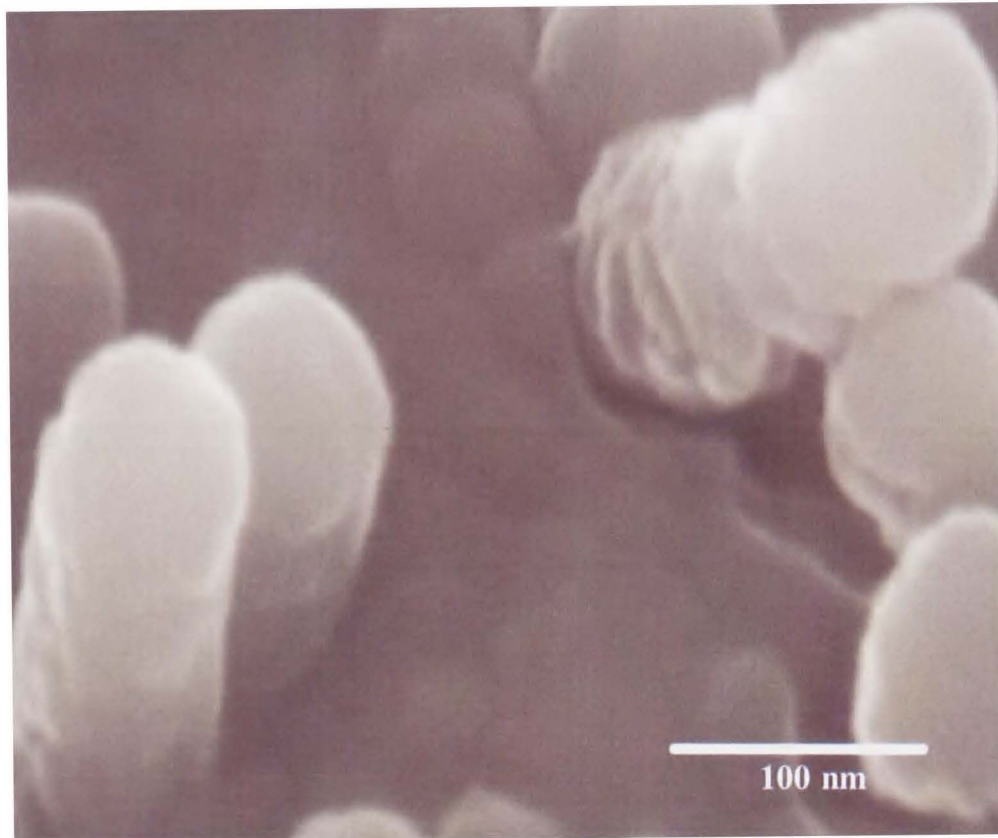


Fig. 6.9. Higher magnification SEM image presenting a closer look of few of the carbon nanotubes protruding from the fractured surface of ABS - 10 wt.% MWCNT. It can be observed that the diameters of the protruding nanotubes vary ~ 40 nm and that the outer surface has a rough appearance probably due to sticking of the glass matrix along the functionalized outer wall.

Fig. 6.10 shows higher magnification SEM images of Vickers indentation induced cracks in MWCNT reinforced ABS glass-ceramics. It can be observed that such cracks are extensively bridged by the reinforcing carbon nanotubes (Fig. 6.10a,b). From observations of a number of cracks it has been estimated that the MWCNTs can bridge a maximum crack opening of ~ 100 nm and start to fracture once the crack opening gets wider (Fig. 6.10c,d). Most of the nanotubes appear to have failed at or near the crack plane. Arrows in Fig. 6.10c point to obviously matching broken halves of the nanotubes protruding from the crack faces. Furthermore, the lengths of nearly

all the fractured nanotubes protruding from the separated crack faces are ~ 50 nm or less (Fig. 6.10d), as was observed in the SEVNB fracture surfaces.

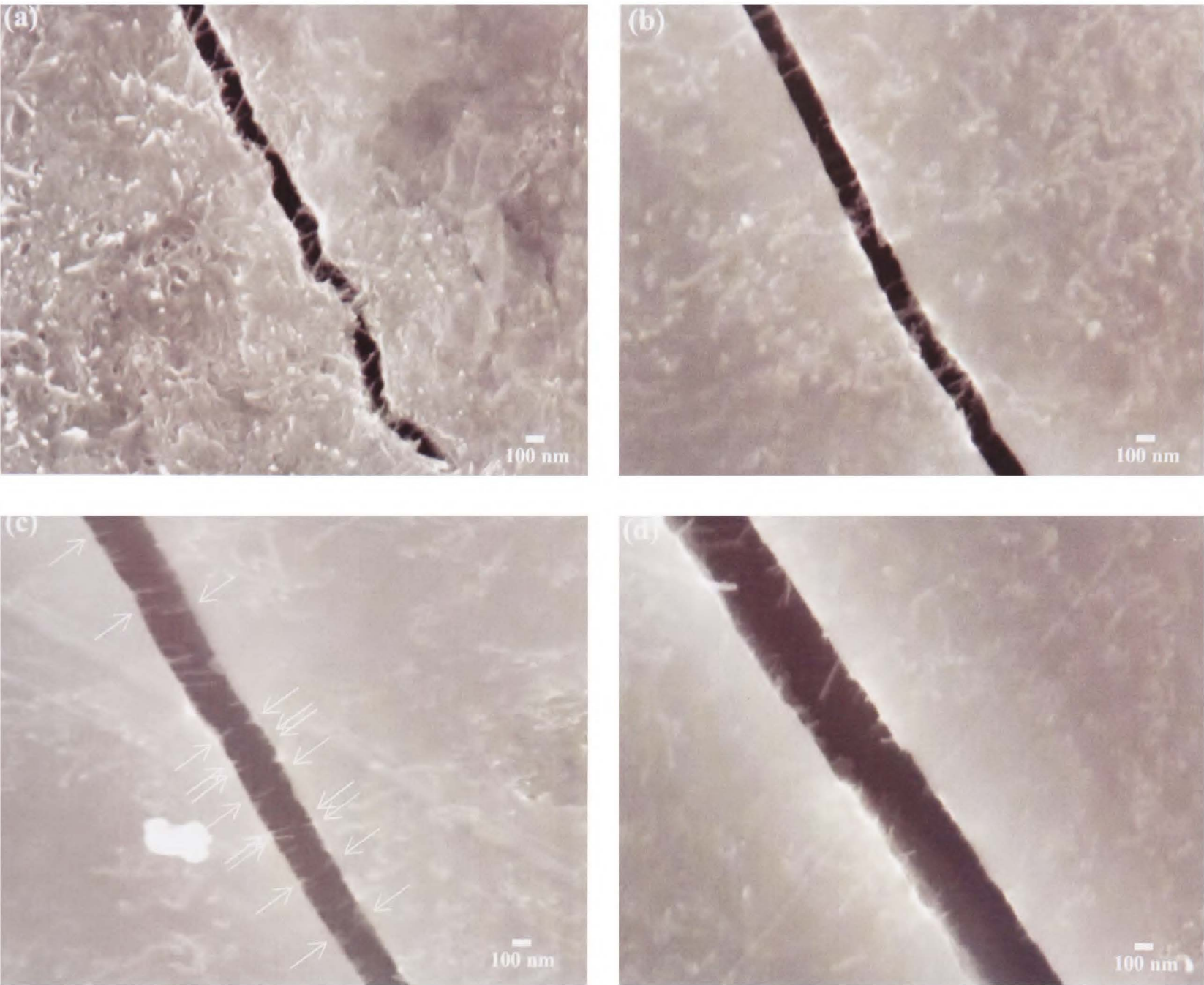
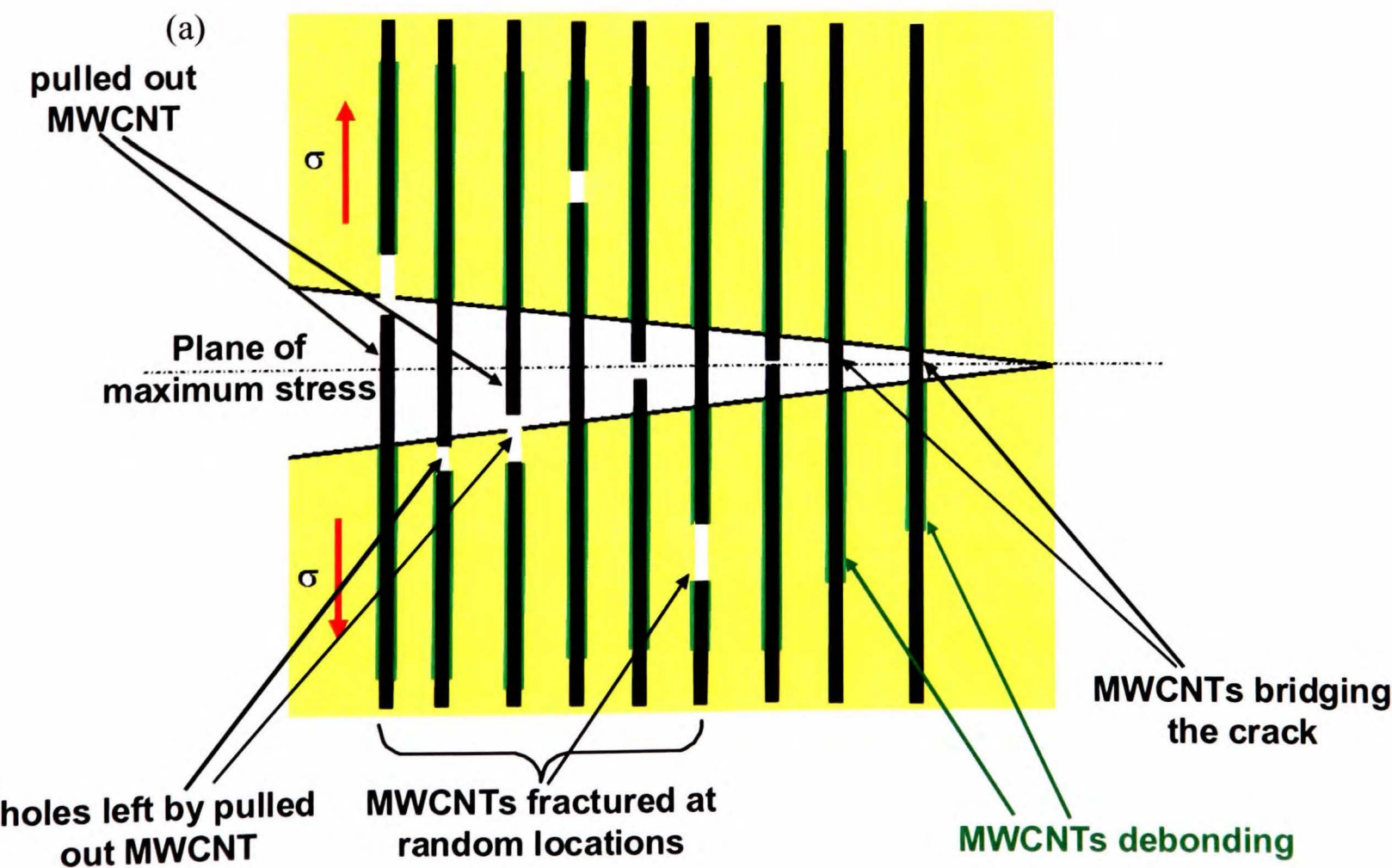


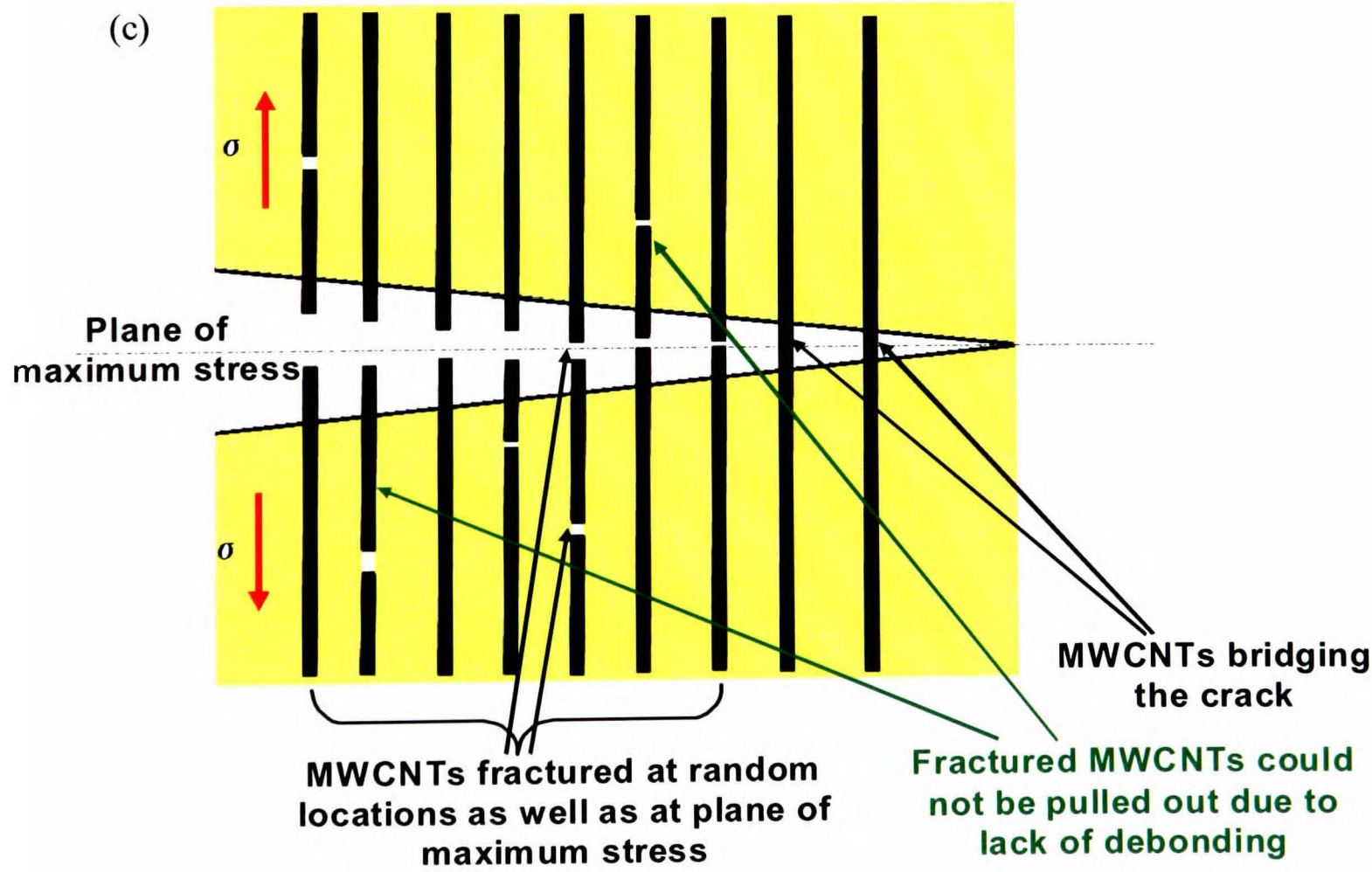
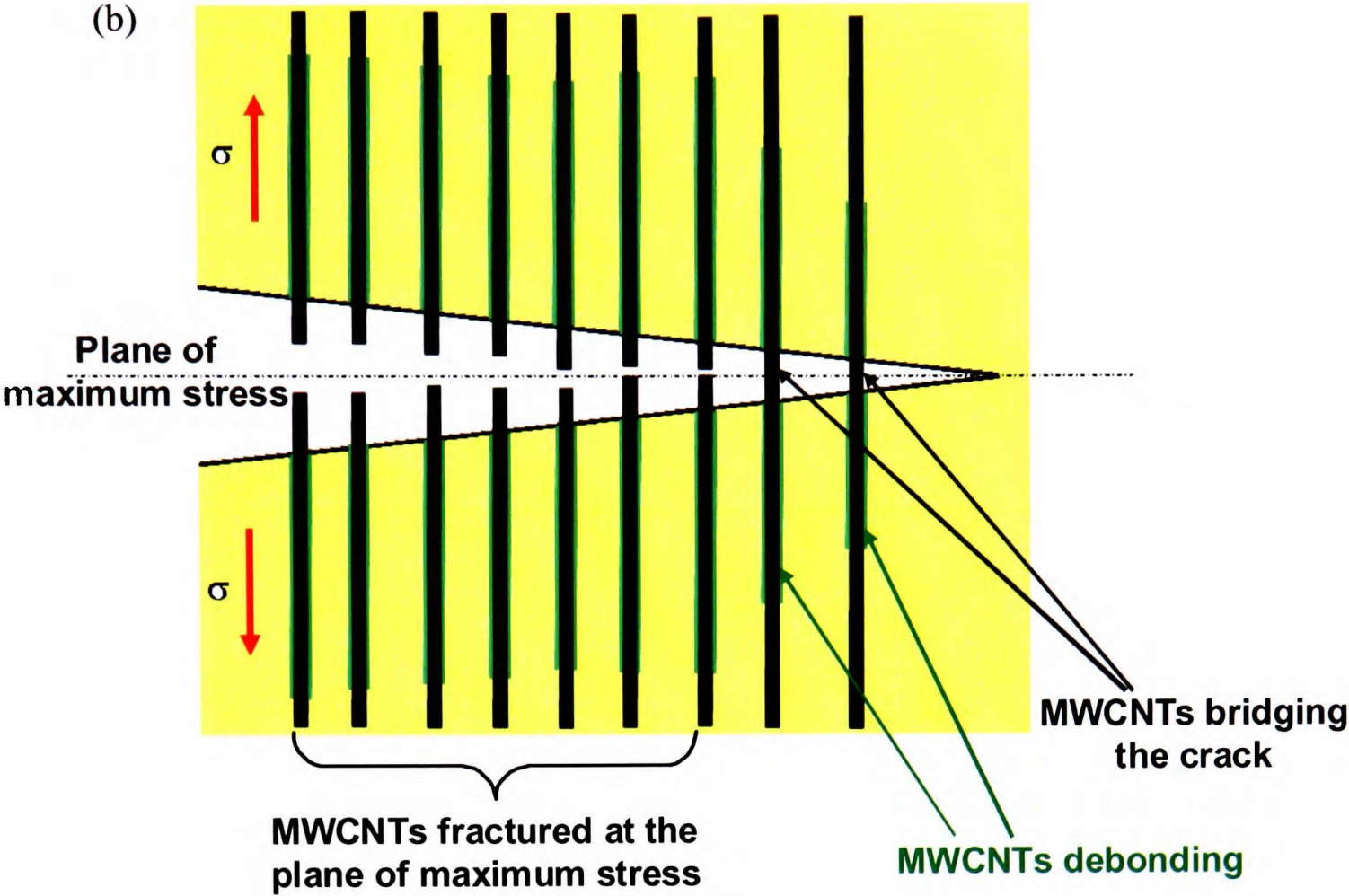
Fig. 6.10. Crack path - MWCNT interactions at different stages of crack propagation in ABS - 10 wt.% MWCNT nanocomposite; (a) and (b) intact carbon nanotubes bridging cracks with opening ~ 100 nm; (c) MWCNTs failing at larger crack openings. Arrows indicate the very obvious evidences of nanotubes failing along the crack plane (plane of maximum stress); (d) very small lengths of nanotubes (≤ 50 nm) protruding from the separated crack faces.

6.2. Discussion

6.2.1. Debonding of MWCNTs during Fracture and Lack of MWCNT Pull-out

Pull-out in fibre reinforced composites is often the most significant toughening mechanism and occurs when the fibres, having defects at random locations along their lengths, fracture some distance away from the plane of maximum stress (the crack plane) during separation of the crack faces (Fig. 6.11a). The lack of holes in the fracture surfaces (Figs. 6.7,6.8 and 6.9) and the observation of many matching pairs of fractured MWCNTs in the indentation cracks (Fig. 6.10c and 6.11b) show that ‘fibre pull-out’, as understood in conventional fibre reinforced composites [24-26], is either minimal or absent in the ABS - MWCNT nanocomposites. The present results show beyond doubt that the MWCNTs fracture between the crack faces as they separate (see Fig. 6.10b and c).





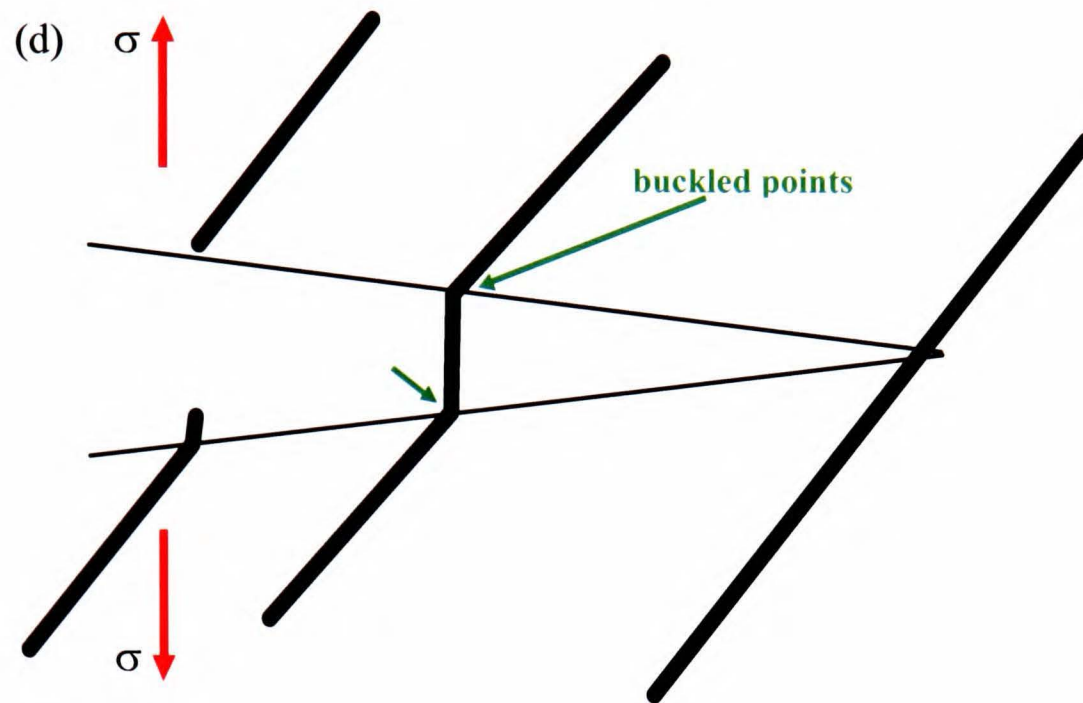


Fig. 6.11. Schematic representations of (a) commonly observed fibre pull-out process; (b) failure of fibre pull-out due to the reinforcing fibres getting fractured at the matrix crack plane (plane of maximum stress); (c) another possible reason for non occurrence of fibre pull-out due to the extremely strong fibre/matrix interface; (d) bridging of crack by fibres not aligned with the stress direction, showing the possibility of such fibres failing at the matrix crack plane due to buckling near the crack plane.

However, from a more classical perspective if we assume that the protruding nanotubes (~ 50 nm) are actually ‘pulled out’ from the matrix and the pull-out process is the major contributor to the composite toughening by $\sim 0.9 \text{ MPa m}^{1/2}$ (for ABS - 10 wt.% MWCNT), the interfacial shear strength (τ) required to provide such toughening is given by [27];

$$\tau = (2d \Delta G_c) / (l_p^2 v_f) \quad (6.1)$$

where ΔG_c ($\sim 24 \text{ J/m}^2$) is the increase in the critical mechanical energy release rate corresponding to the increase in K_{Ic} from $\sim 0.7 \text{ MPa m}^{1/2}$ (unreinforced ABS) to $1.6 \text{ MPa m}^{1/2}$ (for ABS - 10 wt.% MWCNT), d is the diameter of the ‘pulled out’ (~ 40 nm) nanotubes, l_p is the average length of the supposedly ‘pulled out’ nanotubes (~ 50 nm) and v_f corresponds to the volume fraction of the MWCNTs ($\sim 0.1 \approx$ weight

fraction due to similar theoretical densities for ABS and MWCNT). Estimation based on the above equation leads to an unreasonably high value of ~ 2 GPa for τ . This implies that in the case of such short probable ‘pull-out’ lengths, for MWCNT pull-out to be a major contributor to the observed toughening, extremely strong interfaces between the matrix and nanotubes are required, which seem quite improbable from a practical perspective, and especially not consistent with the lack of increase in stiffness (see Fig. 6.5). Hence, along with all the above observations, such theoretical estimation also points to the fact that the contribution of MWCNT pull-out to the toughening recorded for the present ABS - MWCNT nanocomposites is negligible.

One requirement for pull-out to be observed is debonding between the fibre (MWCNT) and the matrix. This enables the fibre to survive the passage of the crack tip past its location in the fracture plane and also aids load transfer, via interfacial friction, to parts of the fibre away from the crack plane, encouraging failure elsewhere followed by pulling out of the failed fibres. The lack of pull-out in the present nanocomposites could therefore have been due to good bonding between the MWCNTs and the matrix. Also, good bonding can even hinder the pull-out of broken fibres, even if they fail at random locations (Fig. 6.11c). However, our observations of a lack of increase in stiffness on incorporation of MWCNT (section 6.1.2) and non occurrence of ‘sword-in-sheath’ type of failure (section 6.1.4) indicate that the glass/MWCNT interface is not too strong. Furthermore, the occurrence of extensive matrix crack bridging (Fig. 6.10a,b) by the reinforcing MWCNT shows that interfacial debonding must occur in the present nanocomposites, and this can be seen directly in Fig. 6.9.

A rough estimate of the debond length can be made using the observation that the MWCNTs tend to fail when the crack opening (c_d) is ~ 100 nm. For a MWCNT

aligned normal to the crack plane and on the point of failure (Fig. 6.12), classical composite theory shows that the stress varies linearly from the fracture stress, σ_f , at the crack plane to a low value at the end of the debonded length. The mean stress in the debonded section (l_d ; assumed to be $\gg c_d$) is therefore, $\sigma_f/2$, and;

$$c_d/l_d = \sigma_f / 2E_f \quad (6.2)$$

where E_f is the Young's modulus of the MWCNTs. With $\sigma_f = 10$ GPa and $E_f = 500$ GPa [15,16], eq. 6.2 gives a debond length of ~ 10 μm . This high value further confirms the effectively weak bonding suggested by the elastic modulus measurements (see Fig. 6.5).

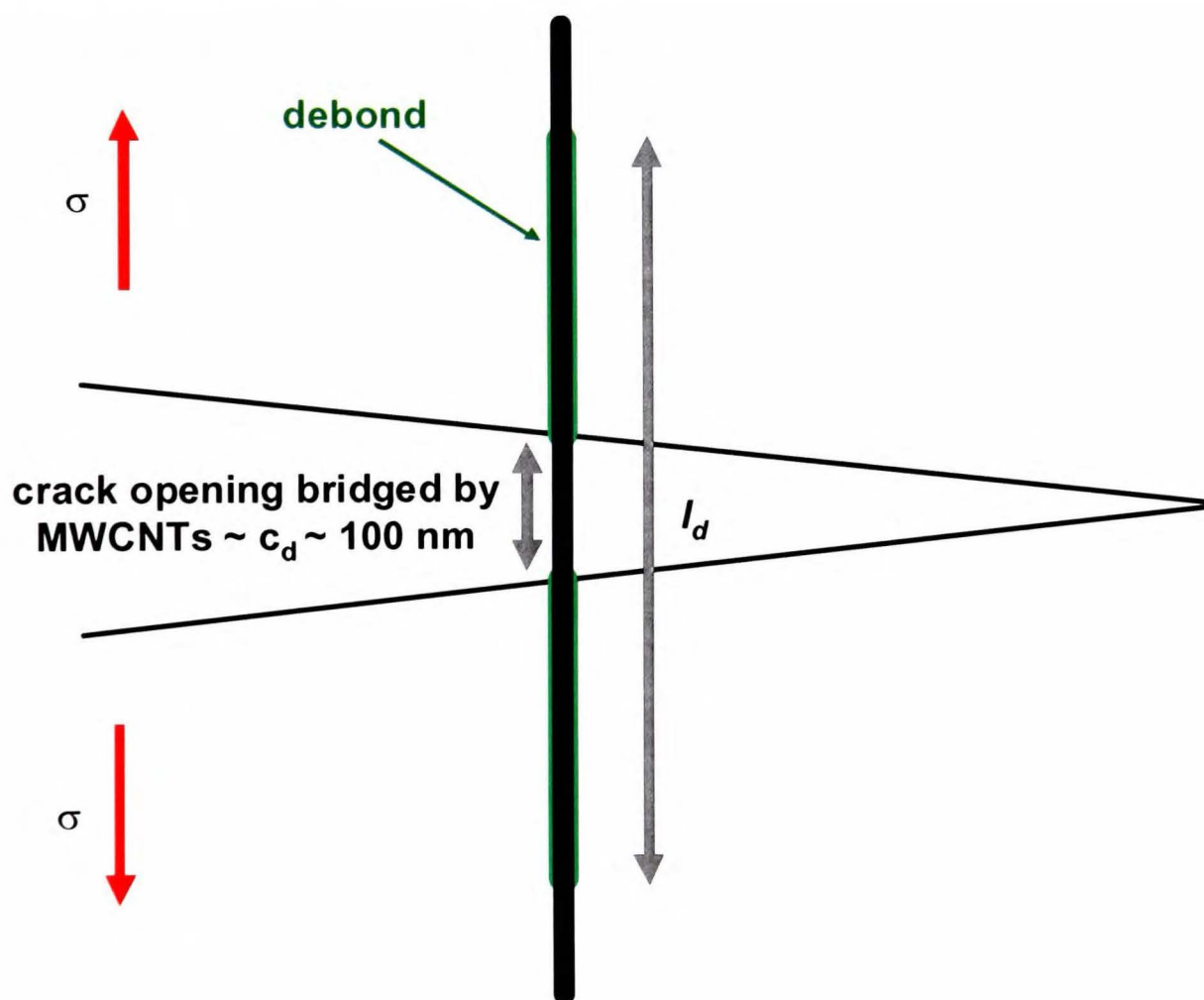


Fig. 6.12. Schematic representation of a nanotube bridging a crack opening of ~ 100 nm (c_d) on getting debonded by a length l_d .

It must be mentioned here that the details of the debonding process in the present nanocomposites are not yet resolved. Fig. 6.9 shows clearly that debonding takes place in the matrix rather than at the actual MWCNT/matrix interface itself,

suggesting that the bonding at the actual interface itself is relatively strong. Indeed, there are persistent reports of silica-based sols and melts showing a strong affinity for CNTs [1,28], wetting them strongly and forming a well-defined coating. Therefore it seems more likely that a strongly bonded and distinct interfacial layer (around the MWCNTs), possibly with composition or structure different to that of the bulk glass, is responsible for this observation. Some perturbation of the glass structure around the CNTs is also evident in Fig. 6.3. However, further experimental work is needed to clarify this issue.

Since effective debonding is evidently easy, albeit within the matrix around the MWCNT, another explanation for the lack of pull-out must be sought. The most fundamental is simply that in the present case the reinforcing MWCNTs possess uniform strength throughout their length, so that they fail at the fracture plane when the stress is at a maximum, resulting in a negligible contribution from MWCNT pull-out to the composite toughening (Fig. 6.11b). The extent to which CNTs are susceptible to fracture at randomly located defects remains to be determined.

Another plausible reason for the lack of MWCNT pull-out in the present ABS - MWCNT nanocomposites is that, in contrast to the case of aligned fibre composites, the MWCNTs are actually in random orientations within the ABS matrix. As a result most of the nanotubes are not orientated parallel to the stress direction during the crack extension. Such random orientations with respect to the stress direction result in buckling of the bridging nanotubes at the point of emergence from the matrix at the crack face (Fig. 6.11d). This is likely to lead to fracture of the reinforcing nanotubes at this point of stress concentration at the crack plane and thus prevent MWCNT pull-out (Fig. 6.11d). Our present hypothesis is also supported by an earlier work in which study of cracks generated in-situ during TEM investigation of randomly oriented

MWCNT reinforced polystyrene composites led to the observation that the nanotubes not aligned perpendicular to the direction of crack propagation tend to fracture at the crack plane, rather than inside the matrix [29].

6.2.2. Theoretical Estimation of Toughening due to MWCNT Reinforcement

SEM observations of the MWCNTs bridging the indentation induced cracks (Fig. 10) reveal that the nanotubes can bridge a maximum of ~ 100 nm of the crack opening (c_d) before themselves getting fractured. Such bridging, followed by fracture of the nanotubes indicates that they provide traction against the crack opening and hence impede crack propagation [26,27,30-32]. In the absence of a significant contribution from MWCNT pull-out, it is important to determine whether this mechanism is sufficient to explain the extensive toughening observed. In the limit of weak interfacial bonding, an estimate for the strain energy that can be released ($G_{bridging}$) in aligned fibre composites can be made by calculating the work done in extending the fibre across the separating crack faces as the fibre debonds [32], as given by the following expression;

$$G_{bridging} = \sigma_f^2 v_f l_d / 3E_f \quad (6.3)$$

where v_f is the volume fraction of the fibres, which can be considered to be same as the wt. fraction of the MWCNTs due to the similar theoretical densities of the matrix (ABS glass) and the multiwalled carbon nanotubes. Eq. 6.3 accounts for the work done against interfacial friction during debonding and the elastic energy stored in the MWCNTs when they fail. For an aligned 10 vol.% MWCNT reinforced nanocomposite, eq. 6.3 gives $G_{bridging} = 67 \text{ J m}^{-2}$. However, considering that in the composites under investigation the fibres are distributed randomly and are not aligned

along the direction of application of stress, the efficiency of the reinforcement is reduced to around one third of their volume fraction [31,33,34], so that our estimate of $G_{bridging}$ is reduced to $\sim 22 \text{ J m}^{-2}$. From the experimentally measured fracture toughness values for unreinforced ABS ($\sim 0.7 \text{ MPa m}^{1/2}$) and ABS - 10 wt.% MWCNT nanocomposite ($\sim 1.6 \text{ MPa m}^{1/2}$), it can be estimated that the fracture of the nanocomposite consumes an additional fracture energy of $\sim 24 \text{ J m}^{-2}$ compared with the unreinforced matrix. We conclude that the observed bridging of the crack interfaces by intact nanotubes is responsible for the vast majority of the observed toughening, and hence the improved strength of the composites. Though the above analysis has revealed that crack bridging by the nanotube reinforcements can lead to a significant increase in fracture toughness, and hence the strength of these MWCNT reinforced ABS nanocomposites, still further improvement is expected if pull-out of the fractured carbon nanotubes can be activated through careful engineering of the interface, or by alignment of the nanotubes so that stress concentrations at the crack are reduced.

6.3. Summary and Outlook

The sol-gel based processing route, followed by hot pressing, allowed for the first time the development of dense ABS - MWCNT nanocomposites containing uniformly dispersed nanotubes up to 10 wt.%. The effective matrix/MWCNT interface was weak, which resulted in inferior stiffness for the nanocomposites. On the contrary, extensive crack bridging by the nanotubes resulted in significant improvement in the fracture toughness and strength over that of the unreinforced ABS glass/ceramic.

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Chapter 7

ELECTRICAL AND THERMAL PROPERTIES OF ABS - MWCNT NANOCOMPOSITES

In addition to acting as stiff fibres for improving the mechanical properties of nanocomposites, multiwalled carbon nanotubes (MWCNTs), which possess very high electrical conductivity ($\sim 1.85 \times 10^3$ S/cm [1]) and thermal conductivity (~ 3000 W m^{-1} K^{-1} [2]) along their lengths, as well as high aspect ratios, can also impart considerable electrical and thermal conductivities to the insulating inorganic materials classes (ceramics) [3-11]. In this light, we report here the effects of MWCNT reinforcement on the electrical and thermal conductivities of the aluminoborosilicate (ABS) glass/ceramic.

7.1. Electrical Conductivity

The electrical resistivities of the hot pressed unreinforced ABS glass/ceramic and the ABS - x wt.% MWCNT nanocomposites ($x = 1.25, 2.5, 5, 10, 15$) were measured using 4-point probe. The corresponding electrical conductivities ($1/\text{resistivity}$) are plotted against the MWCNT contents in Fig. 7.1. It must be noted here that, even though it is difficult to accurately measure the resistivities of insulating materials via 4-probe method, a resistivity of $\sim 10^6$ Ω cm was obtained for the unreinforced glass. This value is comparable with those reported in literature for resistivity of borosilicate glass [3]. Also, similar to the unreinforced glass, there was not enough current flow to obtain accurate readings for the nanocomposites containing 1.25 and 2.5 wt.% MWCNT, and accordingly resistivities of $\sim 10^6$ Ω cm were also measured for them. By contrast, a drastic reduction in resistivity to 1.1 Ω cm was obtained on reinforcement with 5 wt.% MWCNT. Following this 6 orders of magnitude decrease in electrical resistivity (or increase in electrical conductivity), the conductivity

increased with further increase in MWCNT content, albeit at a much lower rate. Hence, a maximum conductivity of ~ 2.1 S/cm was obtained for ABS - 15 wt.% MWCNT nanocomposite, as against the conductivity of $\sim 10^{-6}$ S/cm for unreinforced glass. It must be mentioned here that such conductivity values lie in the semiconductor range, but relatively close to the metallic conductor threshold (10^2 S/cm) [5,12].

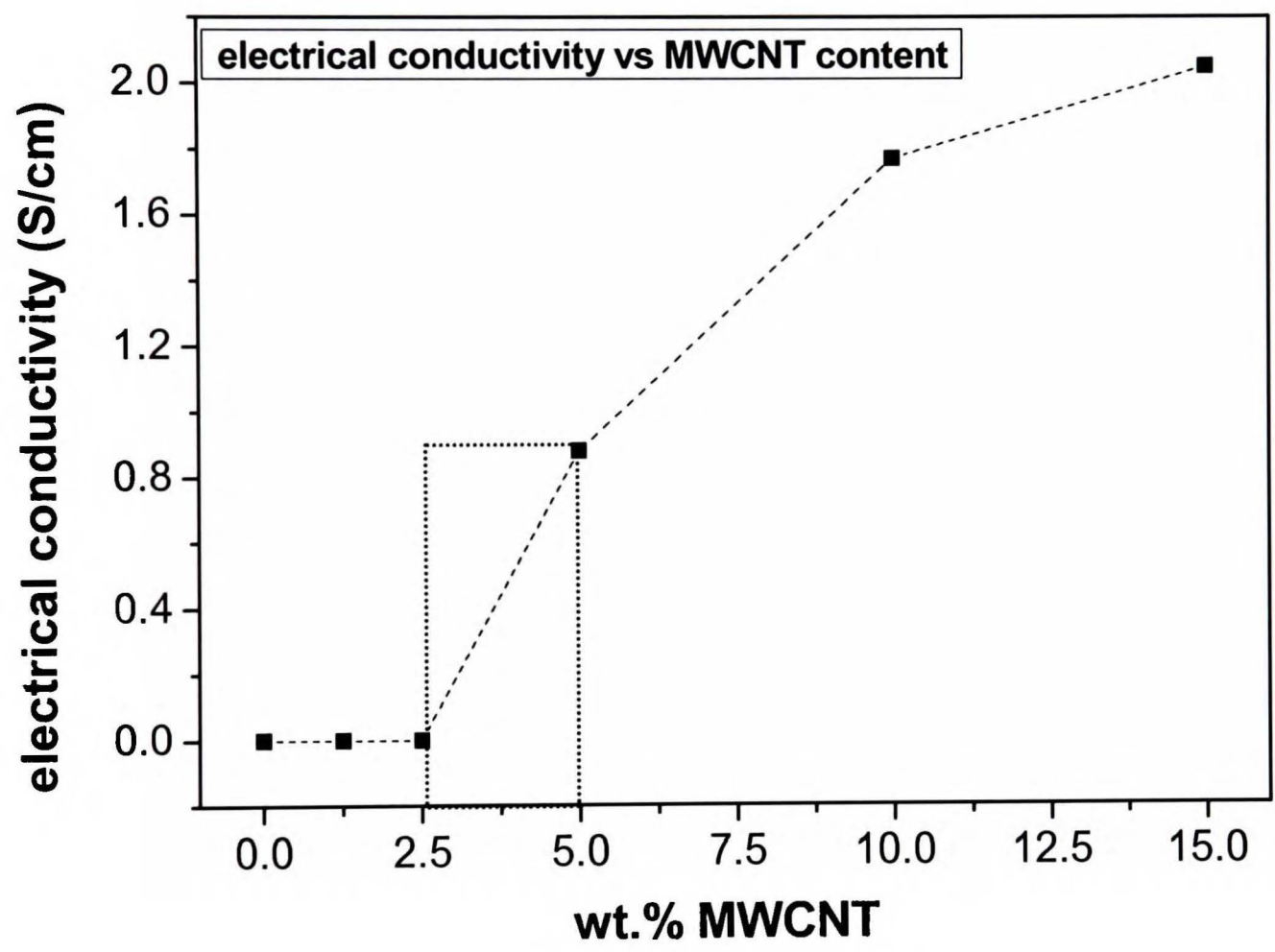


Fig. 7.1. Variation of electrical conductivity with MWCNT content for the ABS - MWCNT nanocomposites. Note that a drastically increased electrical conductivity is recorded with ABS - 5 wt.% MWCNT, with respect to the unreinforced glass and the nanocomposites containing lesser MWCNT.

The important observation from Fig. 7.1 is that MWCNT additions up to 2.5 wt.% do not affect the electrical conductivity of the nanocomposites to any notable extent. It is only the 5 wt.% addition that leads to a dramatic increase in conductivity. Such observation can be explained based on the percolation theory [7,11,13,14] of

conducting fillers in insulating matrix. According to this theory, as the concentration of the electrically conducting MWCNTs increases in the insulating glass matrices, the average distance between nanotubes decreases, and at a critical MWCNT content, called the percolation threshold, a 3 dimensional interconnectivity of MWCNTs in the ABS matrix is formed, which by providing a conducting path through the nanocomposite converts it from electrical insulator to (semi)conductor. From the present observation, the percolation threshold lies between 2.5 and 5 wt.% MWCNT content (shaded region in Fig. 7.1). In a very recently reported work Boccaccini and co workers [4] obtained a slightly lower percolation threshold of ~ 2 wt.% MWCNT in borosilicate glass matrix (BSG). They also reported a maximum electrical conductivity of $\sim 0.5 \text{ S cm}^{-1}$ for BSG - 3 wt.% MWCNT nanocomposite containing well dispersed nanotubes, which is comparable to the value of $\sim 0.9 \text{ S cm}^{-1}$ obtained with the ABS - 5 wt.% MWCNT nanocomposite in the present work. However, in an earlier work [3], the same research group had reported an electrical conductivity of $\sim 0.1 \text{ S cm}^{-1}$ for BSG - 10 wt.% MWCNT nanocomposite, which is an order of magnitude lower than the conductivity of $\sim 1.7 \text{ S cm}^{-1}$ obtained with the presently investigated ABS - 10 wt.% MWCNT nanocomposite. It must be noted here that in the earlier work [3], the nanotubes were not subjected to functionalization and were severely agglomerated in the BSG matrix, as opposed to the present work and the more recent report by Boccaccini and co workers [4]. Hence, the agglomeration of the nanotubes might have decreased the effective aspect ratios and resulted in lower increments in electrical conductivities in the earlier work of Boccaccini and co workers [3]. Even in the present work, it is plausible that agglomeration of MWCNTs above 10 wt.% (see section 6.1.2) results in a reduction in the rate of increase of electrical conductivity with MWCNT content, above 10 wt.% (Fig. 7.1). The effects

of CNT aspect ratios on the electrical conductivities of CNT reinforced nanocomposites have been described elsewhere [15-17].

Percolation thresholds of ~ 1 vol.% CNTs have been observed in some ceramic - CNT nanocomposites [7,11,14]. The slightly higher percolation thresholds in the present nanocomposites might be due to two reasons. Firstly, it has been reported that MWCNTs purified and functionalized under severely oxidizing conditions, such as in concentrated HNO_3 , lead to higher percolation thresholds [18]. We believe that presence of functionalization induced groups along the side walls of the MWCNTs might limit the effective electrical contacts between the interacting nanotubes. Hence, the purification and functionalization of the presently used nanotubes in HNO_3 may partially account for the apparently higher percolation threshold (see chapter 3; section 3.1.2.1). On a different note, it is also believed that good dispersion of the conducting fillers might delay the formation of three dimensional network of conducting paths required for percolation [4,19]. Hence, though the excellent dispersion of the MWCNTs in the present work is beneficial with respect to the mechanical properties (see chapter 6), such dispersion might be partly responsible for increasing the percolation threshold for electrical conductivity. It may also be recalled here that in polycrystalline ceramics - CNT nanocomposites, the nanotubes are mostly present as ropes, confined along the grain boundaries regions [5-7], which might lead to the formation of percolating networks at lower overall volume fractions.

7.2. Thermal Properties

The effects of MWCNT additions on the thermal diffusivities (κ) of ABS glass/ceramics are presented in Fig. 7.2. It can be observed that incorporation of thermally conducting carbon nanotubes results in improvement of the thermal diffusivity for the nanocomposites. κ increases with increasing MWCNT content, specially above 5 wt.%, reaching a diffusivity of $\sim 0.9 \times 10^{-6} \text{ m}^2/\text{s}$ (for ABS - 15 wt.% MWCNT nanocomposite), as compared to the lower diffusivity of the unreinforced glass-ceramic ($\sim 0.65 \times 10^{-6} \text{ m}^2/\text{s}$).

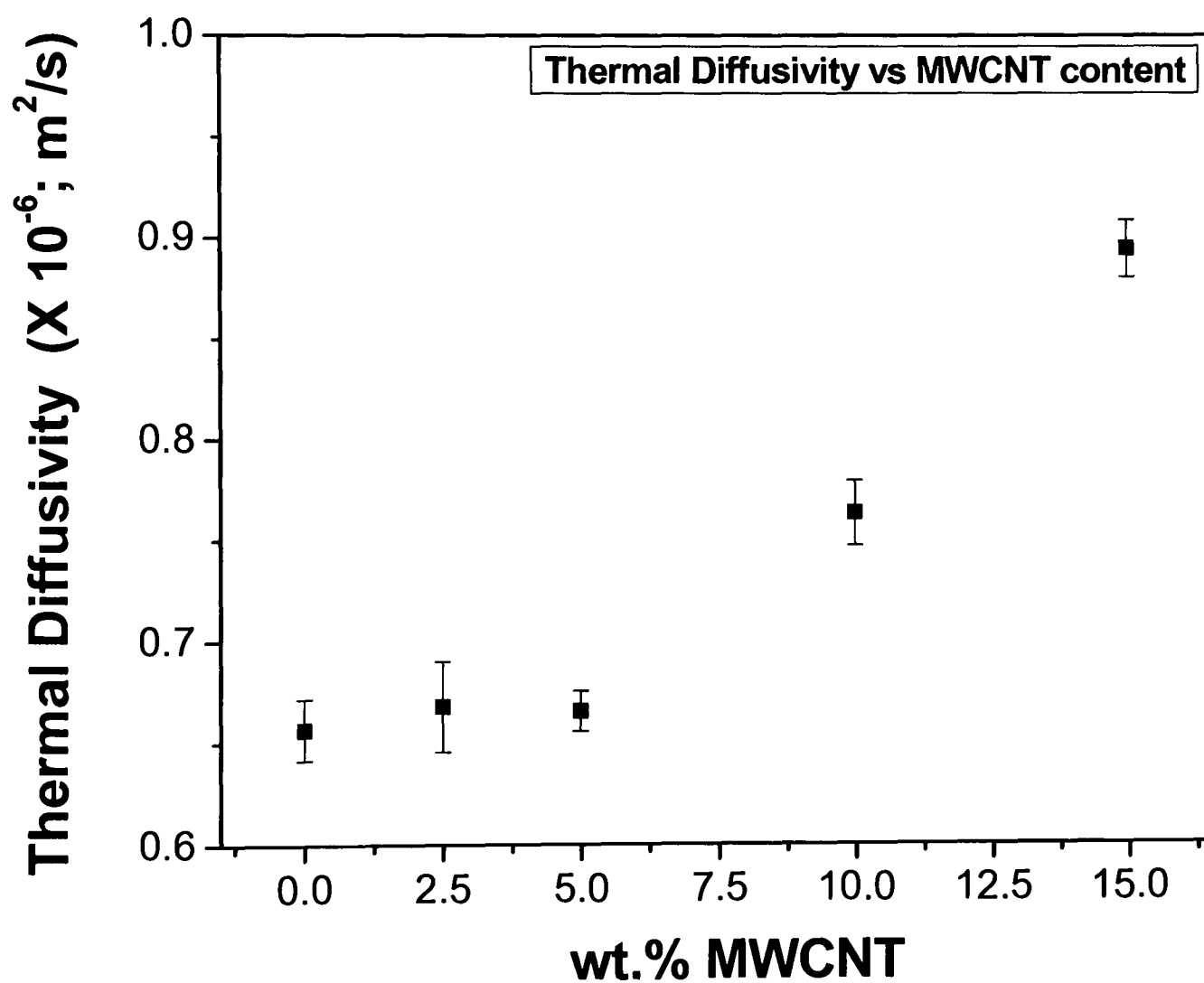


Fig. 7.2. Variation of thermal diffusivity with MWCNT content for the ABS - MWCNT nanocomposites.

Assuming the specific heat capacities of the MWCNTs (c_{pf}) to be $\sim 1 \text{ J g}^{-1} \text{ K}^{-1}$ [20,21] and the matrix (c_{pm}) as $\sim 0.8 \text{ J g}^{-1} \text{ K}^{-1}$ [22], the specific heat capacities (c_p) for the ABS

- MWCNT nanocomposites were calculated using the following relation, based on the rule of mixtures [20];

$$c_p = v_f c_{pf} + (1 - v_f) c_{pm} \tag{7.1}$$

where v_f is the volume fraction of the carbon nanotubes.

The combined values for the thermal diffusivity (κ), specific heat capacity (c_p) and density (ρ) (see chapter 6) were then used to calculate the effective thermal conductivity (K_c) using the following relation;

$$K_c = \kappa c_p \rho \tag{7.2}$$

The effects of carbon nanotube additions on the thermal conductivity of the aluminoborosilicate glass/ceramic are presented in Fig. 7.3. Incorporation of 15 wt.% MWCNT resulted in ~ 40% improvement with respect to the unreinforced glass/ceramic.

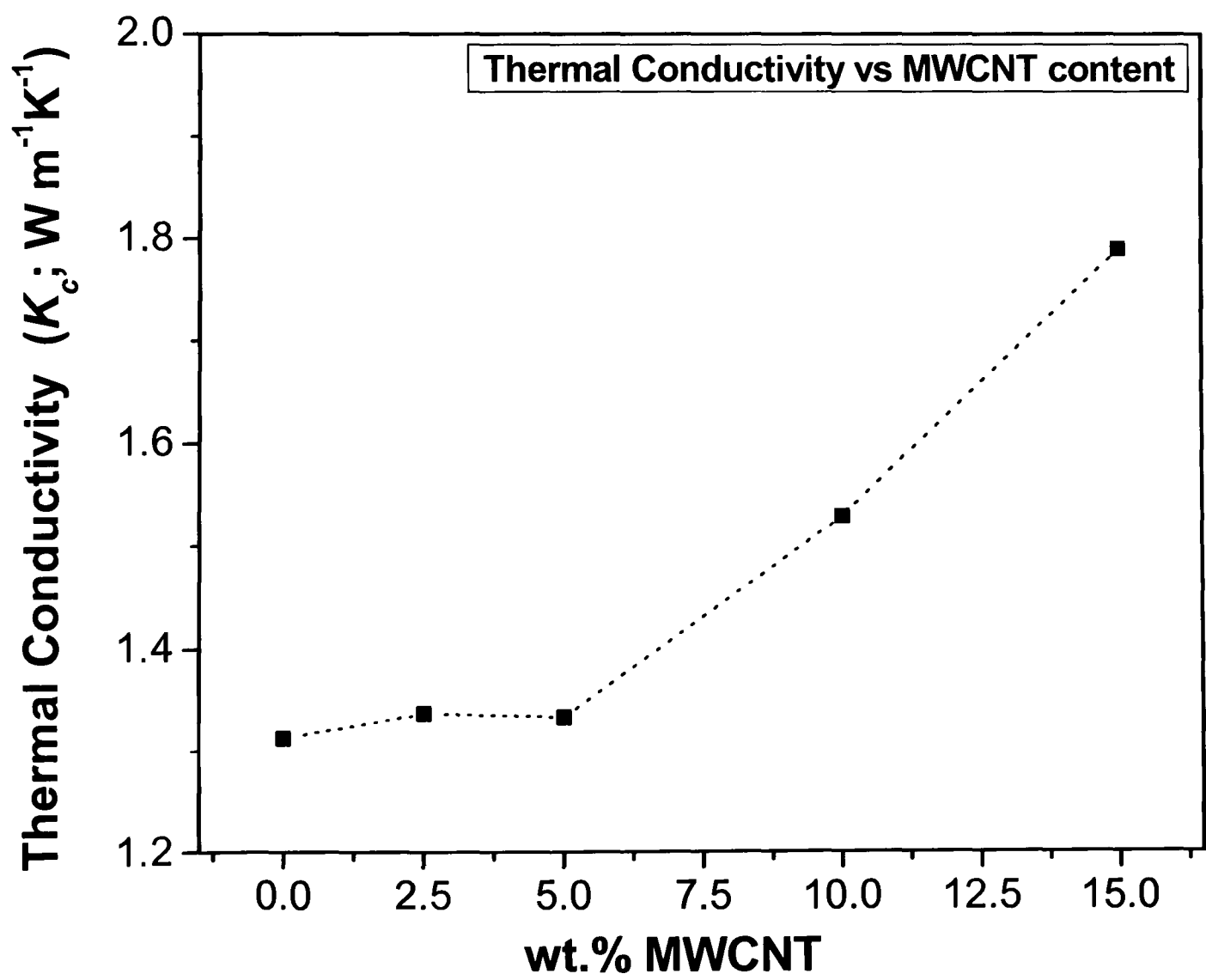


Fig. 7.3. Variation of thermal conductivity with MWCNT content for the ABS - MWCNT nanocomposites.

In the only previous work investigating the thermal conductivity of borosilicate glass - MWCNT nanocomposites [4], a conductivity of $\sim 1.3 \text{ W m}^{-1} \text{ K}^{-1}$ was obtained for a nanotube content of 3 wt.%, which is in agreement with our results for ABS - 2.5 wt.% MWCNT. In the only other report on glass matrix - CNT nanocomposites, Sivakumar et al. [8] reported a $\sim 60\%$ improvement in thermal conductivity on reinforcing SiO_2 with 10 vol.% randomly oriented MWCNTs.

Assuming the thermal resistance at the nanotube/matrix interfaces to be negligible, the thermal conductivity of fibre reinforced composites (K_c) containing randomly oriented fibres (MWCNT) can be estimated as [23];

$$K_c = K_m + 1/3 K_f v_f \quad (7.3)$$

where K_m and K_f are the thermal conductivities of the matrix (ABS) and the MWCNT, respectively. With $K_m = 1.3 \text{ W m}^{-1} \text{ K}^{-1}$ (see Fig. 7.3) and $K_f = 3000 \text{ W m}^{-1} \text{ K}^{-1}$ [2,20], eq. 7.3 yields a value of $K_c = 151.3 \text{ W m}^{-1} \text{ K}^{-1}$ for ABS - 15 wt.% MWCNT. This value is nearly two orders of magnitude higher than the experimentally obtained K_c ($\sim 1.8 \text{ W m}^{-1} \text{ K}^{-1}$). Such a discrepancy between the theoretically estimated and the experimentally observed values for thermal conductivities have also been reported earlier for ceramic - CNT as well as polymer - CNT nanocomposites. The lower thermal conductivities for the CNT reinforced nanocomposites have mainly been attributed to high resistance at the interface between the matrix and the nanotubes, called the Kapitza resistance (R_i) [8,20,24,25]. It must be noted that due to the enormous aspect ratios of the carbon nanotubes and the concomitantly increased volume fraction of interfaces with respect to other fibres, the interface effects become more important in the nanotube reinforced composites.

Based on an effective medium approach (EMA) Nan and co-workers [25] derived the following expression for the thermal conductivity of composites (K_c), which includes the effect of interfacial thermal resistance (R_i) and assumes a random distribution of the reinforcing fibres of length (L);

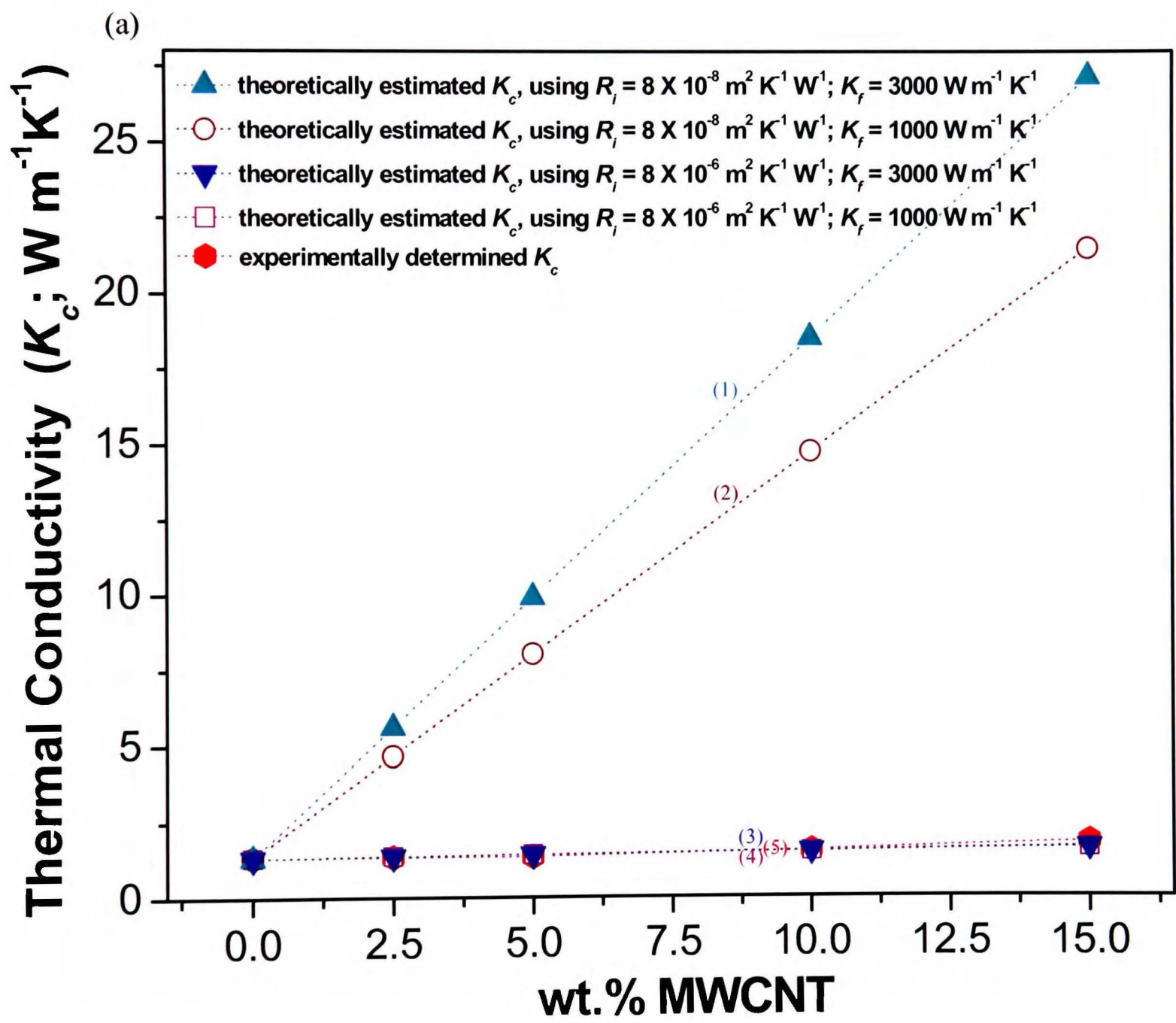
$$K_c = K_m + \frac{K_f L}{2R_i K_f + L} \frac{v_f}{3} \quad (7.4)$$

A value of $\sim 8 \times 10^{-8} \text{ m}^2 \text{ K}^{-1} \text{ W}^{-1}$ was estimated for the interfacial resistance (R_i) in carbon nanotube reinforced organic fluids and polymers [20,26]. Assuming similar value for R_i and $3000 \text{ W m}^{-1} \text{ K}^{-1}$ for the thermal conductivity of the MWCNTs (K_f) the nanocomposite conductivity (K_c) was estimated for the different ABS - MWCNT nanocomposites using eq. 7.4. The simulated curve (1), using these values, is compared with the curve obtained with experimental K_c values (5) in Fig. 7.4a. It can be observed that the simulated curve (1) lies significantly above the curve (5), indicating that the thermal conductivities of the present ABS - MWCNT nanocomposites are inferior (by an order of magnitude) to those estimated using $R_i = 8 \times 10^{-8} \text{ m}^2 \text{ K}^{-1} \text{ W}^{-1}$. In order to further understand the reason behind the lower experimentally obtained K_c values, and in light of an earlier report suggesting that chemical functionalization might lead to reduction in the intrinsic K_f of carbon nanotubes by a factor of ~ 3 [27], curve (2) was generated based on eq. 7.4, assuming a value of $1000 \text{ W m}^{-1} \text{ K}^{-1}$ for the thermal conductivity of the as functionalized MWCNTs used in the present study (see Fig. 7.4a). However, the estimated K_c values were still significantly higher than the experimental values. In this light, curves (3) and (4) were generated assuming a much higher value for R_i ($\sim 8 \times 10^{-6} \text{ m}^2 \text{ K}^{-1} \text{ W}^{-1}$) and the simulated curves appeared to agree relatively well with curve (5), based on the experimentally determined K_c values, irrespective of the value assumed for the intrinsic conductivity of the MWCNTs (see Fig. 7.4a). It must be noted that such high

values for interfacial thermal resistance, which is two orders of magnitude higher than those estimated for organic fluids/polymer - CNT nanocomposites, have also been reported for ceramic (BaTiO_3) - MWCNT in an earlier work [20]. It is often suggested that strong bonding at the interface between the nanotubes and the matrix improves the interfacial thermal conductivity. However, in the present work the effective interface between the MWCNTs and the ABS matrix has been found to be weak (see chapter 6). It is believed that such weak interface partly accounts for the high interfacial thermal resistance and concomitantly limited improvement in the thermal conductivity on incorporation of carbon nanotubes. Hence, the above findings suggest that, among the different reasons limiting thermal transport in fibre reinforced composites, high interfacial thermal resistance contributes significantly towards lowering the thermal conductivities of ceramic - CNT nanocomposites.

It must also be noted here that, eq. 7.4 is based on the rule of mixtures for composites and predicts a linear increase in thermal conductivity with nanotube content. However, the experimental values indicate that there is a significant increase in thermal conductivity for the nanocomposites containing MWCNTs above 5 wt.% (see Fig. 7.3 and 7.4b). We believe that this is also a result of percolation effect of the nanotubes. Furthermore, a magnified view of the region near curves 3-5, as presented in Fig. 7.4b, reveals that though the experimental values lie slightly below the estimated values based on eq. 7.4 (using the higher value for $R_i \sim 8 \times 10^{-6} \text{ m}^2 \text{ K}^{-1} \text{ W}^{-1}$) for nanotube contents ≤ 5 wt.%, the experimentally determined thermal conductivities (curve 5) for the nanocomposites containing more than 5 wt.% MWCNTs rapidly rise to values greater than those predicted by curves (3) and (4). Such behaviour suggests that the interfacial resistance between the nanotubes, which

becomes important beyond the percolation threshold, is lower than the matrix/nanotube interfacial resistance.



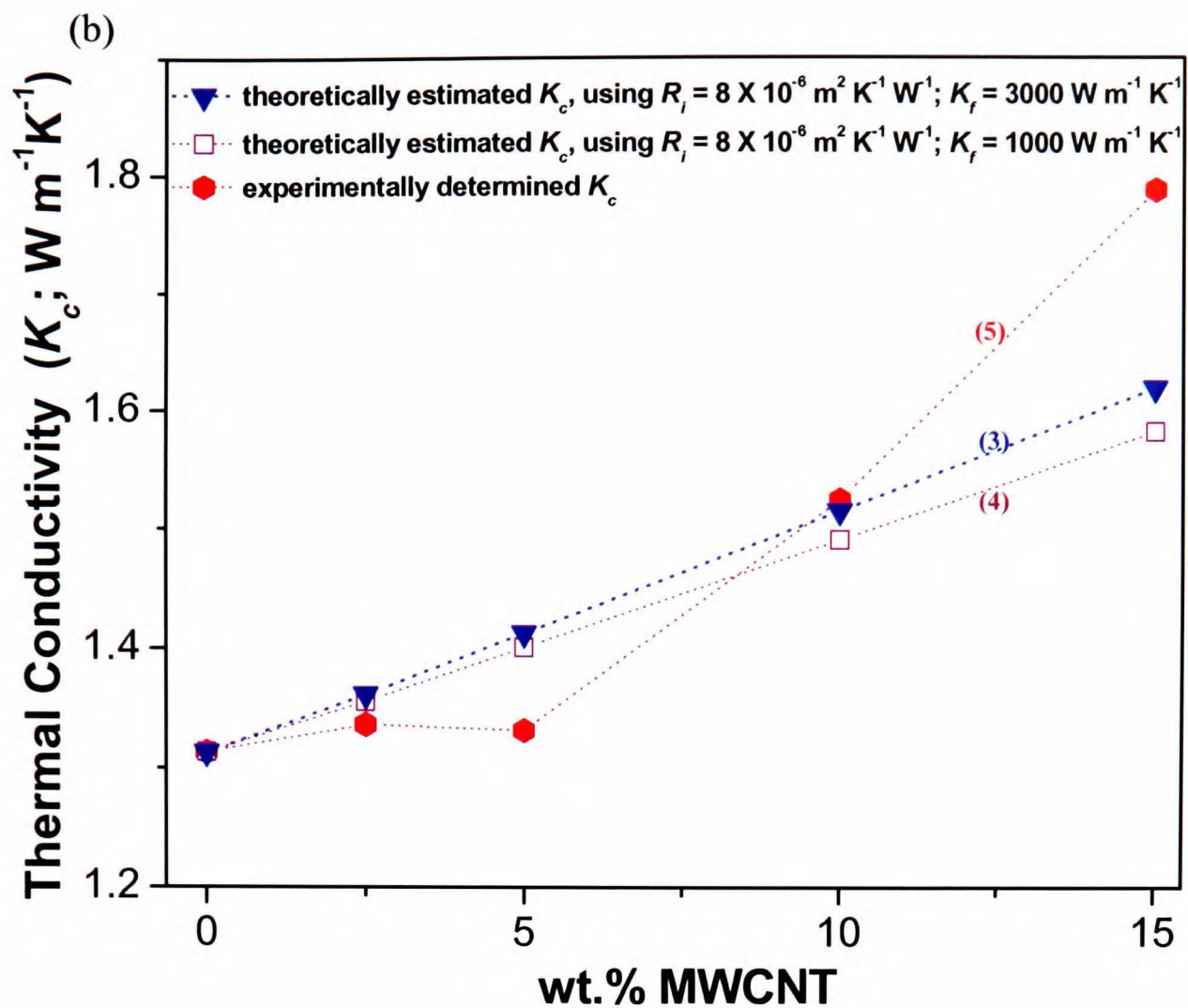


Fig. 7.4. (a) Comparison of the experimentally determined thermal conductivity values, with those estimated using a formulation based on EMA (eq. 7.4) with different values for interfacial resistance (R_i) and intrinsic thermal conductivity of MWCNT (K_f); (b) Magnified view of the region of curves (3), (4) and (5).

7.3. Summary and Outlook

Hence, incorporation of MWCNTs in aluminoborosilicate glass/ceramic results in significant improvement in the electrical conductivities, along with modest improvements in thermal conductivities. It is believed that the improvement in thermal conductivity is limited by resistance at the matrix/CNT interfaces. Nevertheless, such improvements are believed to enhance the applicability of aluminoborosilicate glass, especially in some of the applications in electronic industries [28-30] which demand improved electrical and thermal properties.

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Chapter 8

CONCLUSION AND FUTURE WORK

8.1. Conclusions

The present work was based on two objectives with respect to the two different kinds of ceramic nanocomposites; viz. particulate reinforced polycrystalline Al_2O_3 nanocomposites and multiwalled carbon nanotube (MWCNT) reinforced aluminoborosilicate glass/ceramic (ABS) nanocomposites. With respect to the former, the research aimed at developing a novel and commercially friendly route to develop oxide nanoparticles reinforced Al_2O_3 -based nanocomposites possessing improved mechanical and tribological properties with respect to monolithic alumina. For the ABS - MWCNT nanocomposites, the research explored the feasibility of using a recently developed processing route to fabricate dense nanocomposites containing well dispersed nanotubes up to a relatively high content of 15 wt.%. The effects of MWCNT contents on the mechanical, electrical and thermal properties of the ABS - MWCNT nanocomposites were also investigated. More specifically, based on the observations and the concurrent analysis, the following conclusions have been reached.

8.1.1. Al_2O_3 -based Particulate Nanocomposite

- (a) Pressureless sintering at 1450°C for 5 hrs in air can lead to the development of single phase, homogeneous solid solution of 10 wt.% Fe_2O_3 in Al_2O_3 (solution treatment).
- (b) Heat treatments in reducing atmosphere ($\text{N}_2 + 4\% \text{H}_2$ forming gas mixture) at various temperatures between $1250 - 1550^\circ\text{C}$ for different durations up to 50 h resulted in the precipitation of FeAl_2O_4 out of the solid solution throughout the bulk of the samples (reduction aging).

- (c) Reduction aging at the optimized temperature of 1450°C for 10 - 20 h resulted in the formation of intragranular nanosized particles of FeAl_2O_4 in addition to micron sized particles along the matrix grain boundaries. However, significant coarsening of the second phase particles occurred on aging for elongated time period of ~ 50 hrs or at the highest investigated temperature of 1550°C.
- (d) Within a certain depth from the surface, FeAl_2O_4 got further reduced to metallic Fe during reduction aging. The thickness of this surface layer increased with aging duration up to a maximum of $\sim 100\ \mu\text{m}$ on aging at 1550°C for 50 h.
- (e) The ‘hybrid nano/micro composite’, developed on aging for the optimum duration (between 10 - 20 hrs at 1450°C), possess improved fracture toughness (by $\sim 40\%$) and flexural strength (by $\sim 50\%$) with respect to pure Al_2O_3 .
- (f) The development of compressive residual stress in the matrix due to the coefficient of thermal expansion mismatch between the matrix (Al_2O_3) and the particulates (FeAl_2O_4) and change in fracture mode from intergranular to transgranular in the presence of nanosized intragranular second phase particles are believed to result in the fracture toughness improvement.
- (g) The Al_2O_3 - FeAl_2O_4 nanocomposites developed by reduction aging at 1450°C for durations of 10 and 20 h are more wear resistant as compared to monolithic alumina. However, none of the nanocomposites developed at 1550°C showed any improvement in the wear resistance.
- (h) The presence of yttria (~ 250 ppm) doping further improved the wear resistance of the nanocomposites developed at 1450°C, with the nanocomposite developed after 20 h of reduction aging exhibiting the minimum wear rate, which is significantly less (by a factor of ~ 2.5) than that recorded with monolithic alumina. However, yttria doping did not have any noticeable influence on the

wear rates of the nanocomposites developed at the higher aging temperature of 1550°C.

(i) Suppression of brittle intergranular fracture induced grain pull outs in the presence of intragranular nanosized second phase particles is believed to be the major factor responsible for the improved wear resistance of the nanocomposites with respect to monolithic alumina. However, the coarse micron sized (greater than $\sim 2 \mu\text{m}$) FeAl_2O_4 particles present along the grain boundaries and triple point corners of the matrix grains have been found to be detrimental towards the wear resistance, which is believed to be the main reason for the poorer wear properties of the nanocomposites developed at 1550°C.

8.1.2. ABS - MWCNT Nanocomposites

- (a) The recently developed processing route, involving careful functionalization of MWCNTs, ultrasonication based sol-gel and hot pressing, can produce dense (96-98% ρ_{th}) ABS glass/ceramic - MWCNT nanocomposites with well dispersed carbon nanotubes with contents up to at least 10 wt.%. However, the incorporation of 15 wt.% MWCNT leads to nanotube agglomeration in the composite.
- (b) Reinforcement of the ABS glass/ceramic with 10 wt.% MWCNT results in the improvement of fracture toughness by nearly 150%, along with a doubling of the flexural strength with respect to unreinforced ABS glass/ceramic.

- (c) Carbon nanotubes are observed to bridge crack openings of up to ~ 100 nm, which provides the major contribution to the improvement in fracture toughness.
- (d) However, the nanocomposites do not exhibit significant fibre (MWCNT) pull-out. Observations suggest that this is mainly due to the carbon nanotubes getting fractured at the matrix crack plane, which is the plane of maximum stress, and not at random locations along their length as is required for pull out to occur.
- (e) The nanocomposites possess significantly higher electrical conductivities ($\sim 2.1 \text{ S cm}^{-1}$ for ABS - 15 wt.% MWCNT) with respect to the unreinforced ABS glass/ceramic ($\sim 10^{-6} \text{ S cm}^{-1}$), with a jump of ~ 6 orders of magnitude at the percolation threshold of between 2.5 to 5 wt.% MWCNT.
- (f) The thermal diffusivities and thermal conductivities of the nanocomposites increased with increasing MWCNT contents, reaching a maximum conductivity of $\sim 1.8 \text{ W m}^{-1} \text{ K}^{-1}$ for ABS - 15 wt.% MWCNT, which is $\sim 40\%$ improvement over the thermal conductivity of unreinforced ABS glass/ceramic ($\sim 1.3 \text{ W m}^{-1} \text{ K}^{-1}$). Comparison of the experimentally measured values with those theoretically estimated using effective medium approach revealed that the resistance at the matrix/CNT interfaces (Kapitza resistance $\sim 8 \times 10^{-6} \text{ m}^2 \text{ K}^{-1} \text{ W}^{-1}$) is a dominating influence over the thermal behaviour of the ABS - MWCNT nanocomposites.

8.2. Future Work

The present research investigations, which have achieved the twin objectives of developing particulate reinforced and carbon nanotube reinforced ceramic composites possessing superior properties via novel processing routes, open up opportunities for further work, which may lead to further modification of the processing routes with respect to commercial mass production, result in the development of materials possessing still improved properties and provide better understanding of the roles of nanosized second phase particles and carbon nanotubes as reinforcements for improving the material properties. More precisely, with reference to the present research results, the following work may be undertaken in the near future.

8.2.1. Al₂O₃-based Particulate Nanocomposite

- (a) The major aim behind the development of the present processing route has been to allow commercial processing of oxide/oxide nanocomposites by eliminating the requirements of hot pressing or other advanced processing techniques. In this light, for making the process more commercially friendly, investigations are required to ascertain whether similar or even better results can be obtained on using cheaper and less pure grades of alumina starting powders, using water, instead of ethanol, as the powder dispersing medium followed by spray drying and avoiding the need for quenching the solid solutions following sintering.
- (b) Use of different gas mixtures as the reducing atmosphere may be investigated since the reducing conditions might affect the phase and

microstructural developments, as also the formation of an iron containing surface layer.

- (c) Additional investigations using TEM/HRTEM or other analytical microscopes may be performed to understand the mechanisms behind the microstructural developments, in light of the possible segregation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ during the initial stages of the aging treatments as well as the possible formation of any intermediate phases. Such analytical treatments may also throw more light on the role of the reducing atmosphere in the formation of the nanosized intragranular second phase particles.
- (d) The possible reasons behind the improvement in the wear resistance and the sub-surface damage for the nanocomposites may be elucidated by in detail TEM observations of foils carefully prepared from near the as worn surfaces.

8.2.2. ABS - MWCNT Nanocomposites

- (a) Modification of the processes used for purification and functionalization of the nanotubes might provide an insight into non occurrence of the sword - in - sheath failure and pull out on the fracture surfaces of the MWCNTs used in the present study to reinforce the ABS glass/ceramic. Furthermore, functionalization under less severe oxidizing conditions may be carried out in order to explore the possibility of further improvement in the electrical and thermal properties.
- (b) Raman investigation of the nanocomposites may be carried out to investigate the residual stresses developed in the nanotubes. This might lead to a better

understanding of the reinforcing effects of the MWCNTs in the nanocomposites. However, the weak Raman signal from the nanotubes present in the bulk nanocomposites might be the main hindrance for such investigation.

- (c) The use of advanced sintering techniques like spark plasma sintering (SPS) may be explored in place of hot pressing, since SPS might minimize the possible damage to the nanotubes occurring during hot pressing and also result in cleaner interface, which might have influence on the mechanical and physical properties.
- (d) In the present study it has been observed that nanosized crystalline mullite particles are formed in the borosilicate glass matrix by increasing the alumina content to 22 wt.%. In this light, the possibility of developing mullite - CNT nanocomposites by converting the entire glass to polycrystalline mullite nanoceramics with further alumina additions, may be explored.