JOURNAL OF MATERIALS SCIENCE **35** (2000) 2695–2699

Microstructural influence on the *R*-curve behavior of a 70%Si_3N_4-30% barium aluminum silicate self-reinforced composite

YI FANG, FENG YU, K. W. WHITE
Department of Mechanical Engineering, University of Houston, Houston, Texas 77204-4792, USA
E-mail: yfang@jetson.uh.edu

Fracture toughness and crack growth resistance (*R*-curve) behavior of several microstructures of 70%Si_3N_4-30%BAS composite are characterized using the indentation and modified compact tension methods, at room temperature. Both the whisker morphology and matrix properties contribute to the fracture resistance behavior. Crack deflection, whisker bridging and pullout are regarded as the dominant toughening mechanisms. © *2000 Kluwer Academic Publishers*

Silicon nitride (Si_3N_4) ceramics have high strength at elevated temperatures, good thermal shock resistance, and relatively good resistance to oxidation [1]. It has been shown that *in situ* grown β-Si_3N_4 whisker reinforcements can significantly increase the fracture resistance over monolithic ceramics. Some exhibit *R*-curve behavior [2–5], which has been shown to contribute to improved reliability [6–8]. However, their formidable price due to high processing cost precludes their application to many engineering structures. To address this problem, the research community has expended much effort toward economical approaches to microstructural development of damage tolerant materials.

Recent work [9–12] has shown that β-Si_3N_4 whiskers can be grown *in situ* from α-Si_3N_4 in the presence of liquid Barium Aluminum Silicate (BAS), with the composition of $BaO\cdot Al_2O_3\cdot 2SiO_2$, by pressureless sintering. Our previous study [13] indicated that the Si_3N_4/BAS self-reinforced composite with a nearly completely crystallized BAS matrix, exhibited high fracture strength at both room and high temperature. The flexural strength of this composite could reach 950 MPa at room temperature and 790 MPa at 1120°C, which matched those of the conventional hot-pressed silicon nitride ceramics. This study intends to characterize the fracture resistance behavior of this composite, through identification of the contribution from both the BAS matrix and β-Si_3N_4 whisker morphology to *R*-curve behavior.

70 vol.% Si_3N_4 powder (UBE, E-10) was mixed with 30 vol.% BAS constituent powders: $BaCO_3$, Al_2O_3 and SiO_2, in isopropanol for 48 hours. Green pellets were compacted at a pressure of 50 MPa. Samples were sintered for 5, 30, 60, 120 and 240 minutes, respectively, all at 1920°C in 1 atm N_2. The density of as-sintered samples was measured by the water immersion method. Phase characterization by X-ray diffraction was performed on the bulk material. The whisker morphology was characterized from sintered samples etched in molten NaOH or by plasma etching method. The diameter (D) and the length (L) of at least 1000 whiskers were measured from samples processed under each condition on SEM micrographs. The apparent aspect ratio and average length of whiskers were calculated in the method proposed by Braue *et al.* [14] and Wotting *et al.* [15]. Indentation toughness estimations were used to calculate the fracture toughness according to the Anstis approach [16]. The samples processed at 1920°C for 30 minutes, 120 minutes and 240 minutes were tested using a modified compact tension (M-CT) specimen at room temperature to determine the *R*-curve behavior, by the compliance method.

A typical microstructure of this composite was shown in Fig. 1. β-Si_3N_4 whiskers appear randomly oriented in a fine, continuous matrix of BAS. The average whisker length, as shown in Fig. 2, increased from 1.1 μm to 3.8 μm with extension of sintering time, whereas the whisker aspect ratio increased to a maximum at 120 minutes perhaps indicating onset of large scale whisker impingement. In this composite, BAS not only served as a liquid phase sintering aid to promote the α to β phase transformation, but also remained as a structural matrix. Since the BAS volume fractions of up to 30% are used, the role of this matrix strongly influenced the composite properties. XRD results showed the persistence of some residual α-Si_3N_4 phase in samples sintered at 1920°C for 5 and 30 minutes. Complete α to β transformation was obtained in samples sintered for at least 60 minutes. As expected for these composites, only the hexagonal allotrope of BAS matrix was identified from the X-ray diffraction spectra.

Only coarser microstructures (sintered for 120 and 240 minutes) showed rising *R*-curve behavior (Fig. 3). The fine microstructure, characteristic of materials sintered at 1920°C-30 minutes, did not exhibit rising fracture resistance curve, as expected from the average

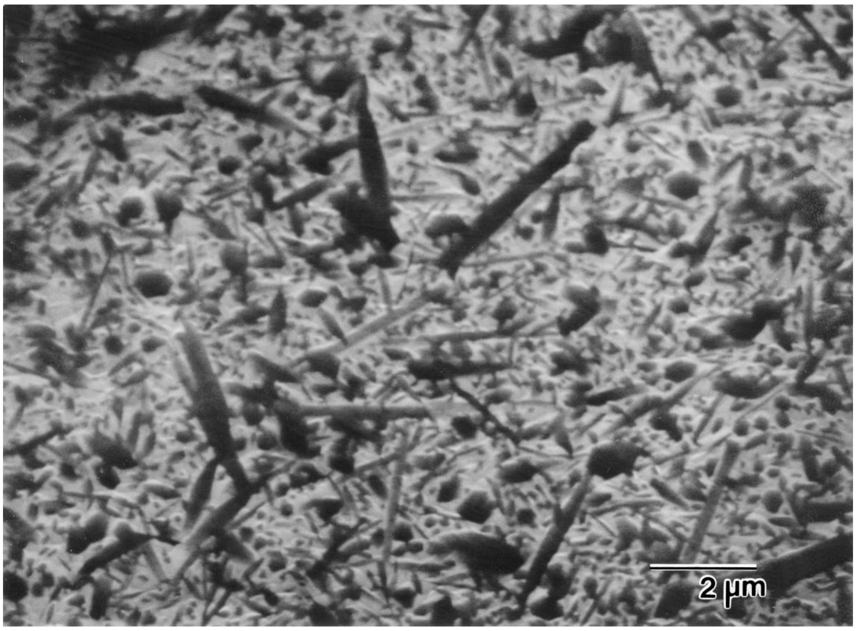

Figure 1 Plasma etched 1920°C 120 min sample surface shows the general morphology of composite.

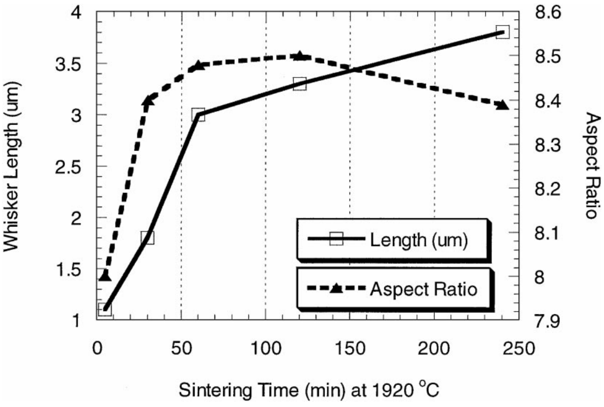

Figure 2 Calculated average whisker length and average apparent aspect ratio of whiskers as a function of sintering time.

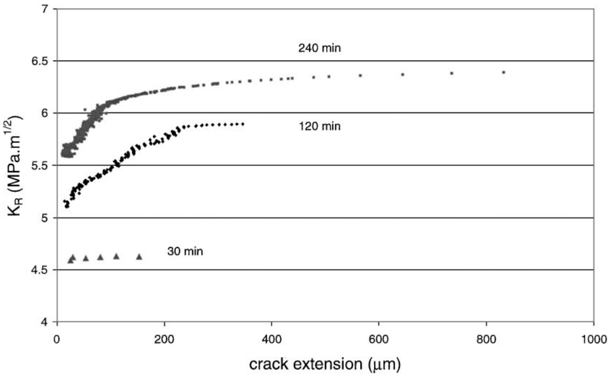

Figure 3 Crack growth resistance curve for the samples sintered at 1920°C 30 min, 120 min and 240 min. For references, the indentation fracture toughness results are 30 min: 4.9 ± 0.1 MPa·m$^{1/2}$, 120 min: 5.4 ± 0.1 MPa·m$^{1/2}$ and 240 min: 6.3 ± 0.1 MPa·m$^{1/2}$.

whisker length about 1.8 μm and the incomplete $\alpha-\beta$ transformation. When the average whisker diameter increased from 0.21 μm to 0.46 μm and also the average length was elongated from 1.8 to 3.8 μm, the initial points of R-curves increased from 4.6 to 5.6 MPa·$\sqrt{}$m. Crack deflection most likely contributed to this increment. As a non-cumulative toughening mechanism [17, 18], crack deflection is mainly the reaction of the crack tip with microstructure [19]. Particles with rod-shaped morphology are predicted to be the most suitable for maximizing toughening. Therefore, the β-Si_3N_4 whisker is favored to acquire better toughening effect. In our composites, due to the incomplete $\alpha-\beta$ transformation, the crack deflection toughening in 1920°C-30 min sample was not as effective in the samples with fully transformation and its crack initiation value was the lowest. After fully transformation, more rough crack deflection profile was observed with the whisker coarsening on 240 min sample and caused the further increase on the starting point of R-curve behavior. This was confirmed by the SEM observation of fracture surface of M-CT samples (Fig. 4).

Becher *et al.* [17, 20], also White and Guzzone [21] attributed the rising of fracture resistance curve in SiC whisker reinforce alumina mostly to frictional bridging and pullout mechanisms. The initial rising region of the R-curve, primarily due to bridging mechanism, would be strongly affected by the whisker diameter. And the second stage of R-curve was predominantly controlled by pullout in which the bigger the whisker diameter, the greater fracture resistance on longer crack extension, but the diameter of whisker had negligible effects on the rate of increase in the R-curve [20]. Following the theoretical prediction, the major toughening mechanisms in this composite were whisker bridging and pullout mechanisms as well. And coarser whisker morphology in this composite enhanced the toughening effects. When the sintering time was elongated from 120 min to 240 min, the average whisker diameter increased from 0.38 μm to 0.46 μm and the R-Curve of 240 min samples had steeper initial rising part which agreed well with Becher's prediction on bridging mechanism. However, the total rising of R-Curve of 240 min sample (0.7 MPa·$\sqrt{}$m) is minor comparing with the increase in

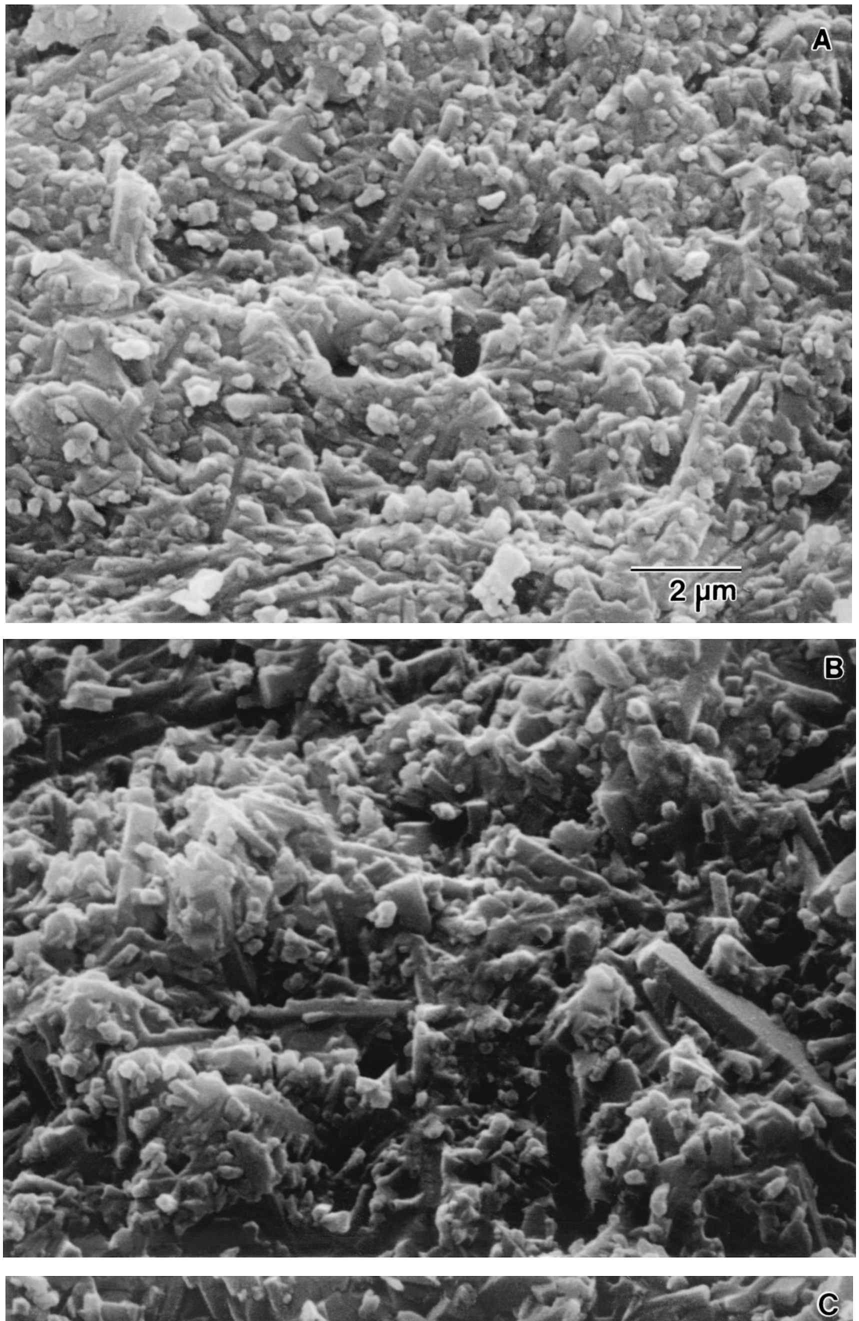

Figure 4 M-CT sample fracture surface of (A) 30 min, (B) 120 min and (C) 240 min.

120 minutes sample (0.6 MPa·$\sqrt{}$m). Noting the slight decrease of whisker aspect ratio of 240 minutes sample in Fig. 2, it indicated the onset of the large scale whisker impingement. Whisker impingement, causing whisker surface defects, hurt the mechanical performance of the whiskers and induced premature whisker fracture on/even before the process of whisker pullout. Therefore, *R*-Curve behavior was largely diminished.

Compared with other Si_3N_4 materials, no whisker longer than 10 μm or wider than 2 μm was found in present samples. This resulted in a relatively small fracture resistance increase (<1 MPa·$\sqrt{}$m) with several hundred micron crack extension.

Generally fracture resistance in whisker reinforced composites was comprised of contributions from both matrix and whisker reinforcement effects. The matrix contribution arose largely from matrix grain bridging effect in the crack wake [17, 22]. Although this is true for the case of high strength structural ceramic matrices like Al_2O_3 and Si_3N_4 [22, 23], it is not expected for this fine grain sized BAS. This glass-ceramic matrix contained predominantly hexacelsian, which no constitutive data existed. However, the data from monoclinic BAS phase, celsian, that was reportedly very low toughness (<2 MPa·$\sqrt{}$m) and strength (<150 MPa) at room temperature [9, 24] and generally low value for glass ceramic, suggest that the hexacelsian BAS acts as a weak phase. Furthermore, since the BAS grain size is predominantly sub-micron [11, 12], not much wake zone contribution to the *R*-Curve is expected from such small size grains. Therefore, the BAS matrix grain bridging has negligible effect on the *R*-Curve behavior. In addition, as BAS matrix acted as liquid sintering aid in 1920°C and crystallized in furnace in the same cooling rate, we thought, the difference in the bonding between silicon nitride and BAS was minor. Therefore, different whisker morphology rather than BAS matrix and interface effect caused the different *R*-Curve behaviors of samples.

Even though, BAS matrix acted as a weak phase, it was important in second aspects to the properties of the composite. The relatively lean whisker content (70 vol%), compared with the conventional pressure sintered Si_3N_4, allowed for the development of microstructures with significantly less impingement, which mean the much more smooth whisker surfaces and whisker pullout favored [25, 26].

The thermal expansion coefficient mismatch between the grain boundary phase and whiskers has been shown to influence the fracture toughness of silicon nitride [27] and other composite [28]. It was also reported that pull-out contributions were markedly diminished in SiC whisker reinforced mullite and soda-lime-glass-matrix composites which have comparable thermal expansion coefficients with that of SiC, as compared with the alumina based composite [17]. The thermal expansion coefficient for hexagonal BAS ($8.0 \times 10^{-6}/°C$) significantly exceeds that of β-silicon nitride ($3.3 \times 10^{-6}/°C$) [9], implying that tensile stresses should dominate at the interface and compressive stresses in the silicon nitride grains. This condition most likely contributes to the promotion of crack deflection, the formation of bridging grains and also enhancement of whisker pullout. The indentation crack on the 1920°C 120 minutes specimen (Fig. 5), exemplified the crack deflection and bridging characters in the wake zone, where the β-Si_3N_4 and BAS matrix is the preferred crack path.

Fig. 6 showed behavior of room temperature fracture toughness with whisker diameter. Indentation fracture toughness increases from 4.6 to 5.3 MPa·$\sqrt{}$m corresponded to a whisker diameter increase from 0.14 μm to 0.36 μm (Fig. 6). The completion of the α to β-Si_3N_4 phase transformation and the increased whisker aspect ratio (shown in Fig. 2), contributed to this toughness improvement according to the crack deflection and bridging model [17, 19]. Further improvements to 6.28 ± 0.11 MPa·$\sqrt{}$m were resulted from coarser microstructure with longer sintering time. This trend with

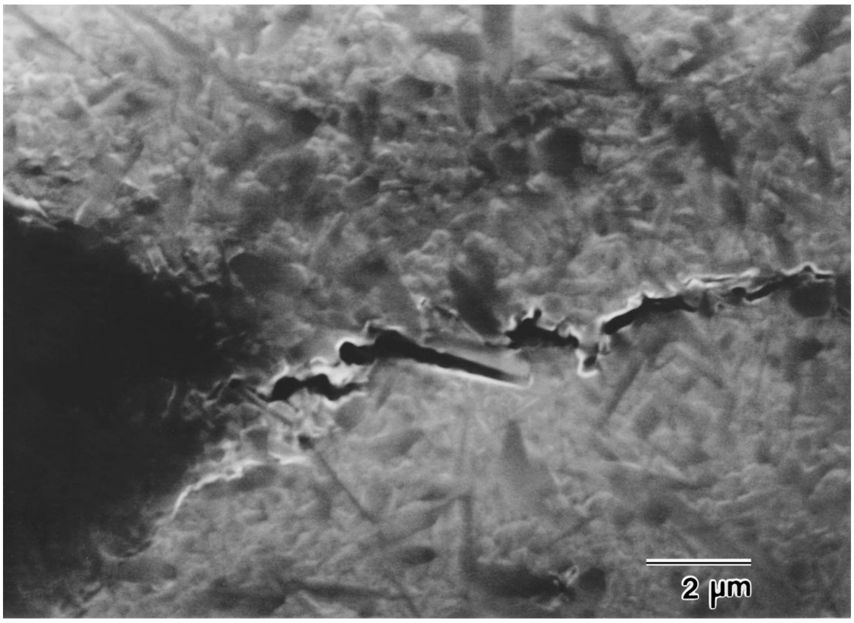

Figure 5 Indentation crack on the 1920°C 120 minutes specimen shows the crack deflection, bridging mechanisms.

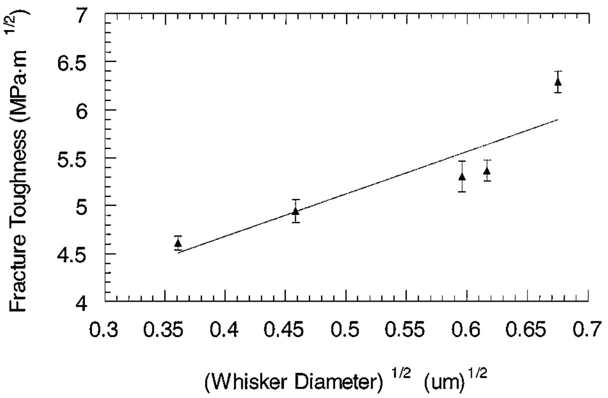

Figure 6 Fracture toughness of the composites sintering at 1920°C as a function of (whisker diameter)$^{1/2}$.

whisker diameter agreed well with bridging models in the literature in which toughness increased linearly with the square root of whisker diameter [17].

As conclusion, in 70%Si_3N_4-30%BAS self reinforced composite, rising R-curve behaviors were identified in samples processed under 1920°C 120 and 240 minutes. The whisker deflection, bridging and pull-out in the crack wake were believed to be the major toughening mechanisms. As a result, the β-Si_3N_4 whisker morphology had a strong influence on the R-Curve behavior. Although the BAS ceramic-glass phase acted as a weak phase in the composite, it enhanced the R-Curve behavior as well by promoting the interfacial cracking between BAS matrix and Si_3N_4 whiskers.

References

1. G. ZIEGLER, J. HEINRICH and G. WOTTING, *J. Mater. Sci.* **l22** (1987) 3041.
2. C. W. LI, D. J. LEE and S. C. LUI, *J. Amer. Ceram. Soc.* **75**(7) (1992) 1777.
3. C. W. LI and J. YAMANIS, *Ceram. Eng. & Sci. Proc.* **10**(7) (1989) 632.
4. N. RAMACHANDRAN and D. K. SHETTY, *J. Amer. Ceram. Soc.* **74**(10) (1991) 2634.
5. Y. W. KIM, M. MITOMO and N. HIROSAKI, *J. Mater. Sci.* **30** (1995) 5178.
6. R. F. COOK and D. R. CLARKE, *Acta Metall.* **36**(3) (1988) 555.
7. K. KENDALL, N. M. ALFORD and J. D. BIRCHALL, *Mater. Res. Soc. Symp. Proc.* **78** (1987) 181.
8. D. K. SHETTY and J. S. WANG, *J. Amer. Ceram. Soc.* **72**(7) (1989) 1158.
9. K. K. RICHARDSON, D. W. FREITAG and D. L. HUNN, *ibid.* **78**(10) (1995) 2662.
10. S. W. QUANDER, A. BANDYOPADHYAY and P. B. ASWATH, *J. Mater. Sci.* **32** (1997) 2021.
11. F. YU, N. NAGARAJAN, Y. FANG and K. W. WHITE, *Ceramic Transactions* **85** (1998) 381.
12. F. YU, C. R. ORTIZ-LONGO, K. W. WHITE and D. L. HUNN, *J. Mater. Sci.* **34** (1999) 2821.
13. F. YU, N. NAGARAJAN, Y. FANG and K. W. WHITE, *J. Amer. Ceram. Soc.*, accepted.
14. W. BRAUE, G. WOTTING and G. ZIEGLER, *Ceramic Microstructure* **86** (Role of Interfaces) (1987) 883.
15. G. WOTTING, B. KANKA and G. ZIEGLER, "Non-Oxide Technical and Engineering Ceramics" Elsevier Science Pub., (1986) p. 83.
16. G. R. ANSTIS, P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **64**(9) (1981) 533.
17. P. F. BECHER, *ibid.* **74**(2) (1991) 255.
18. R. W. STEINBRECH, *J. Europ. Ceram. Soc.* **10** (1992) 131.
19. K. T. FABER and A. G. EVANS, *Acta Metall.* **31**(4) (1983) 565.
20. P. F. BECHER, C. H. HSUEH, K. B. ALEXANDER and E. Y. SUN, *J. Amer. Ceram. Soc.* **79**(2) (1996) 298.
21. K. W. WHITE and L. GUAZZONE, *ibid.* **74**(9) (1991) 2280.
22. P. F. BECHER, JR E. R. FULLER and P. ANGELINI, *ibid.* **74**(9) (1991) 2131.
23. C. Y. CHU and J. P. SINGH, *Ceram. Eng. & Sci. Proc.* **11**(7) (1990) 709.
24. J. J. BUZNIAK and K. P. LAGERLOF, *Ceramic Transactions* **38** (1993) 789.
25. P. SAJGALIK, J. DUSZA and M. J. HOFFMANN, *J. Amer. Ceram. Soc.* **78**(10) (1995) 2619.
26. T. AKATSU, Y. TANABE, S. MATSUURA, H. ISHII, M. MUNAKATA, M. YAMADA, and E. YASUDA, *J. Ceram. Soc. of Japan* **99**(5) (1991) 431.
27. I. M. PETERSON and T. Y. TIEN, *J. Amer. Ceram. Soc.* **78**(9) (1995) 2345.
28. M. TAYA, S. HAYASHI, A. S. KOBAYASHI and H. S. YOON, *ibid.* **73**(5) (1990) 1382.

Received 28 July
and accepted 14 December 1999