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Slurry processing for fabrication of SiC whisker-reinforced Si_3N_4 composites

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In order to solve the major problems of processing whisker-reinforced ceramic composites, such as agglomeration of whiskers, correlation between pH and viscosity has been carefully investigated in a mixed slurry of whiskers and matrix powder. SiC whiskers and Si_3N_4 powder were dispersed homogeneously by controlling pH in aqueous suspension, and the state was successfully fixed by a sudden change of pH to make the slurry more viscous. The slurry was then filtrated rapidly and dried. The strength of hot pressed composites obtained by this procedure was scarcely lowered, with increased whisker loading in the range 0–30 wt% and fracture toughness increased more than 75%.

1. Introduction

Although ceramics have been used in some structural applications, they are well known to be brittle materials. The inherent brittleness of ceramics is one of the main obstructions against further development of such applications. To improve this situation, some toughening methods have been investigated. Incorporation of secondary phases, such as particles and/or whiskers (fibres), has been carried out actively [1–3]. Especially, whisker-reinforcement is considered [4] to be more effective than particle reinforcement in crack deflection toughening [4, 5] due to the acicular (needle-like) shape. Other toughening mechanisms, whisker pull-out and bridging, have been also proposed [6] for composites reinforced by whiskers.

In the present study, the method of achieving uniform dispersion of SiC whisker (SiC_w) in the Si_3N_4 matrix was investigated, in conjunction with careful examination and evaluation of the prepared sintered bodies.

2. Experimental procedure

The diameter and length of SiC whiskers (TWS-400, Tokai Carbon) used were 0.5–1.0 μm and 15–60 μm respectively; they have smooth surfaces without joints. The crystalline form of the whiskers was β-type. Their impurities are shown in Table I. Purity and particle size of the starting powders are shown in Table II. Two matrix compositions were tried for the experiment as shown in Table III. In series I, YA was Si_3N_4 containing Y_2O_3 and Al_2O_3 as sintering aids. In series II, YZ contained Y_2O_3 and ZrO_2 as sintering aids.

As a popular method for dispersing SiC_w in the Si_3N_4 matrix, pH adjustment in an aqueous slurry was carried out [7–8]. As shown in Fig. 1, the zeta potential of the Si_3N_4 particle and SiC_w can be easily controlled by pH adjustment. The zeta potentials of Si_3N_4 and SiC_w are very close, having isoelectric points near pH = 4. When the pH of mixed slurry of Si_3N_4 particles and SiC whiskers is adjusted to be identical in sign and large in absolute difference, electrostatic repulsion can develop and SiC_w can be uniformly dispersed in the Si_3N_4 matrix. However, it is difficult to dry the powder maintaining the dispersed state with uniformly dispersed whiskers.

TABLE I Impurities of SiC whisker

Element	Wt %
O	0.130
Fe	0.055
Ni	0.015
Co	0.205
Ca	< 0.010
Cr	< 0.010
Mg	< 0.010
Al	0.065
Mn	< 0.010

3. Results and discussion

3.1. Effect of slurry processing on the performance of the composites

Fig. 2 [9, 10] shows the cutting edge of Al_2O_3–SiC_w tool (Greenleaf designation WG-300), after interrupted cutting operation [high speed (400 m min^{-1}) turning of grey cast iron bar with four longitudinal grooves]. As seen in the micrograph, catastrophic failure of the edge was avoided by whisker

TABLE II Purity and particle size of starting powders

Material	Particle size (μm)	Purity (%)	Manufacturer and grade
Si_3N_4	0.1–0.3	> 97.000	UBE industries, SN-E10
Y_2O_3	0.4	> 99.990	Nippon Yttrium
Al_2O_3	0.3	> 99.995	Sumitomo Chemicals, AKP-50
ZrO_2	0.4	> 99.900	Tosoh, TZ-0

TABLE III Composition of matrix

Experimental series	Designation	Composition (wt %)
I	YA	94.4 Si_3N_4–3.6 Y_2O_3–2 Al_2O_3
II	YZ	89 Si_3N_4–10 Y_2O_3–1 ZrO_2

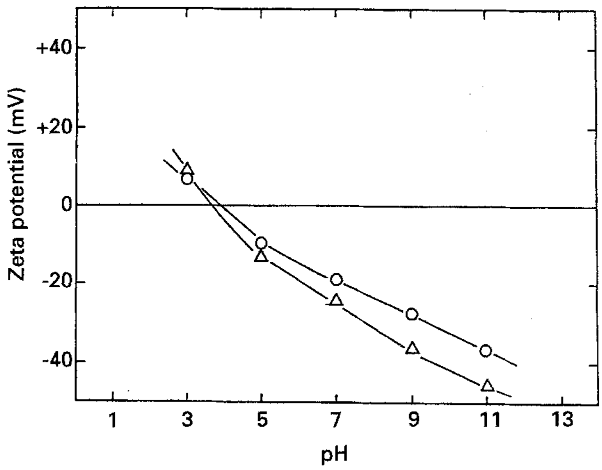

Figure 1 Relation between zeta potential and pH for Si_3N_4 (○) powder and SiC (△) whisker in aqueous slurry.

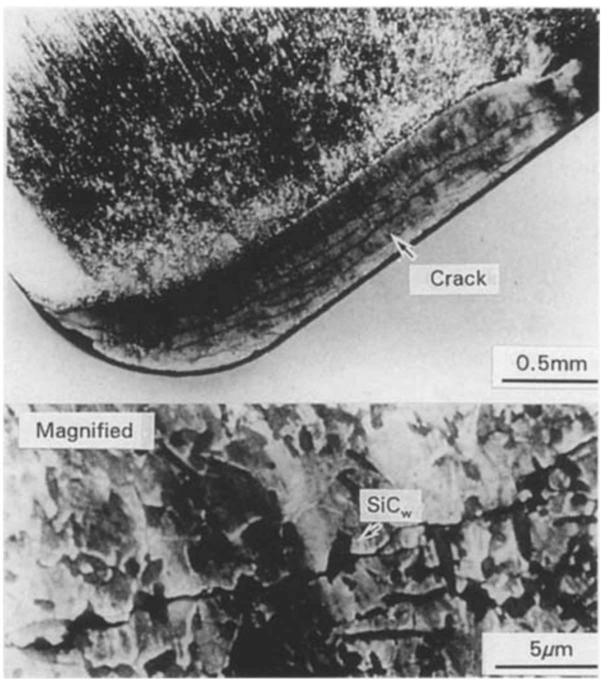

Figure 2 Cutting edge of Al_2O_3–SiC_w tool.

incorporation. Crack deflection along whiskers and bridging of whiskers are also observed. These composites, however, experience some processing difficulties. Namely, whiskers tend to agglomerate easily to each other due to their shape, and the agglomeration lowers sinterability and caused degradation of the mechanical properties of the composite, when it remains in the sintered body. Fig. 3 shows agglomeration in the Al_2O_3–SiC_w composite: the white phase is matrix Al_2O_3, and the dark phase is SiC_w. Pores, a few microns in size occur in the vicinity of the agglomeration. These agglomerations act as the origin of fracture when the composite is stressed. Thus, uniform dispersion of whiskers in the matrix is a key to obtaining sound whisker-reinforced composites.

Initially, two different methods of blending were tried. Fig, 4 shows micrographs of hot pressed bodies prepared by these two methods. One is spray drying and the other is filtration, after adjusting pH to 11 in which good dispersion is achieved. Then, both blends were hot pressed under the same conditions. For the spray dried composite, agglomerations formed by separation of the whiskers matrix during spray drying. The room temperature strength of the composite was lower than that of the Si_3N_4 matrix by 200 MPa. In the filtrated composite, whisker deficient areas up to 50 μm diameter in size were present. Whisker agglomerations were also observed and their strength were much reduced. During filtration, since whiskers precipitate faster than the matrix powder, a whisker enriched layer and a matrix layer were formed. Thus, only by adjusting slurry pH to 11, could a blend with homogeneously dispersed whiskers be obtained. (As an alternative method, an attempt was made to fix the well dispersed state temporarily using the viscosity change.)

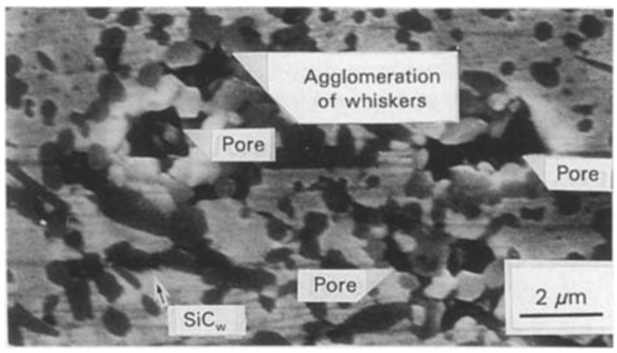

Figure 3 Agglomeration of whiskers in Al_2O_3–SiC_w composite.

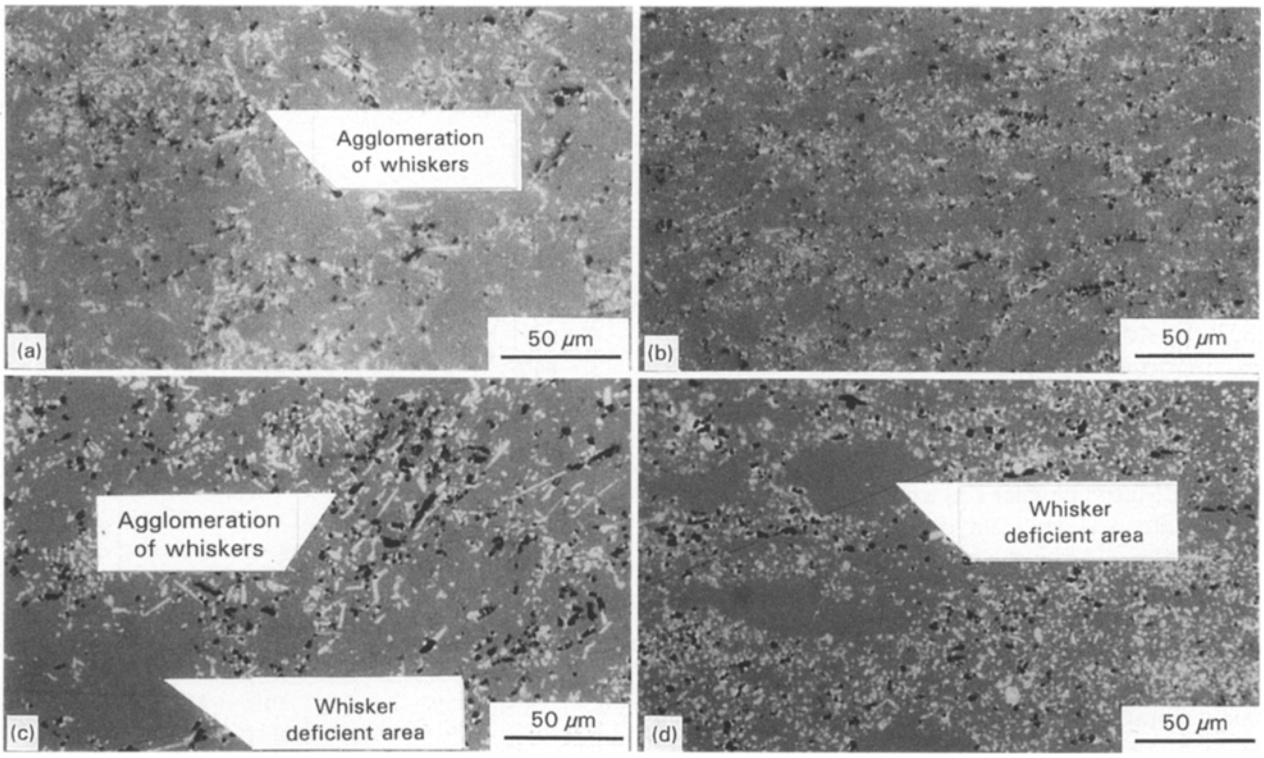

Figure 4 Optical micrographs of Si_3N_4–20 wt % SiC_w composite prepared by conventional methods: (a) spray dried after adjusting to pH 11 [normal to hot pressing (HP) axis]; (b) spray dried after adjusting to pH 11 (parallel to HP axis); (c) filtrated after adjusting to pH 11 (normal to HP axis); and (d) filtrated after adjusting to pH 11 (parallel to HP axis).

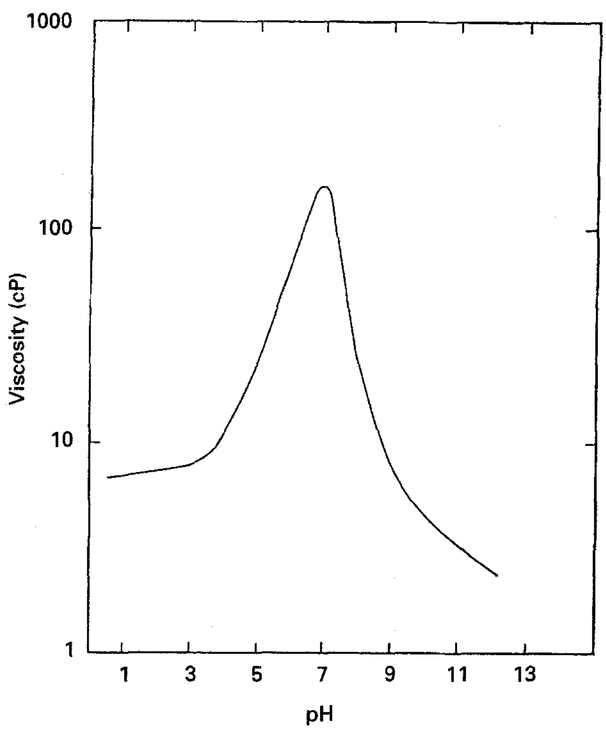

Figure 5 Relation between pH and viscosity for the aqueous mixed slurry of Si_3N_4 and SiC whisker.

The viscosity of the Si_3N_4–SiC_w mixed slurry changes with pH as shown in Fig. 5. In the slurry at pH 11, whiskers are dispersed homogeneously be electrostatic repulsion, and viscosity of the slurry is still low. When the slurry pH is rapidly changed from 11 to 7, the slurry rapidly becomes viscous and prohibits the relative motion of Si_3N_4 particles and SiC whiskers. Therefore, the dispersed state of the whiskers in the matrix powder is fixed temporarily. Fig. 6 explains

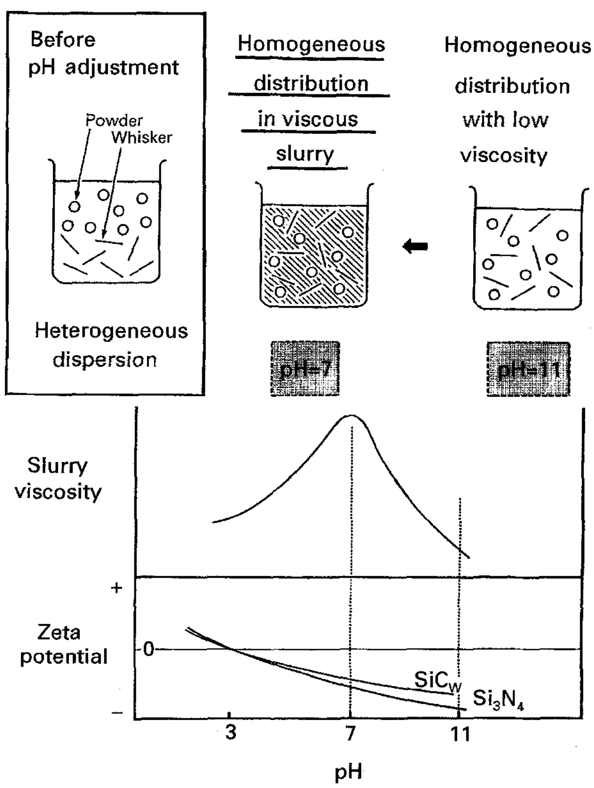

Figure 6 Slurry processing for dispersion.

this method schematically. Before pH adjustment, powders and whiskers are not dispersed homogeneously in the slurry. When the slurry pH is adjusted to 11 and mixed, whiskers are homogeneously dispersed in slurry with low viscosity. After that, by changing the pH to seven rapidly, the viscosity of the slurry increased steeply, and the homogeneously dispersed state was fixed in the slurry.

3.2. Sintering and evaluation of sintered bodies prepared by the optimum method

3.2.1. Preparation

Fig. 7 shows the flow chart of the newly developed process. Matrix powder and whiskers were mixed with water into a slurry, and the pH of the slurry was adjusted to 11. The slurry was mixed by ball milling for 1 h to disperse the whiskers. The pH of the slurry was adjusted to 11, again to disperse whiskers. Then the pH was changed rapidly to seven, and the slurry became viscous. During these two operations, ultrasonic vibration was applied to maintain the dispersed state. The viscous slurry was filtrated by suction and dried. The dried lump was crushed by a mortar.

Blended powders were hot pressed at a pressure of 40 MPa in an atmosphere of N_2 gas. In the course of hot pressing operation, the temperature was kept at 1873 K (1600 °C) for 1 h and 2043 K (1770 °C) for 2 h. Hot pressed composites were evaluated by the following four items: density, by the water displacement (Archimedes') method; fracture toughness (JIS R1607); three point flexural strength (JIS R1601); and observation of microstructure using the optical microscope, scanning and transmission electron microscopes.

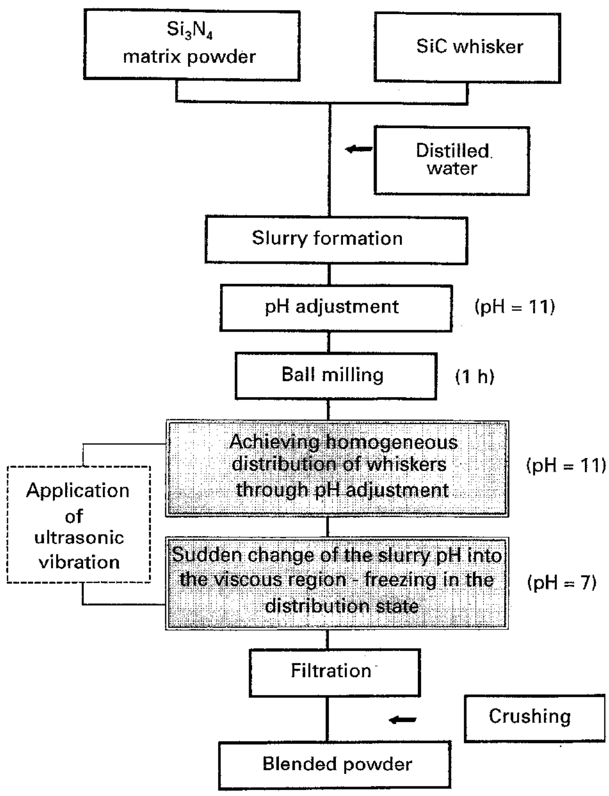

Figure 7 Flow chart of the process.

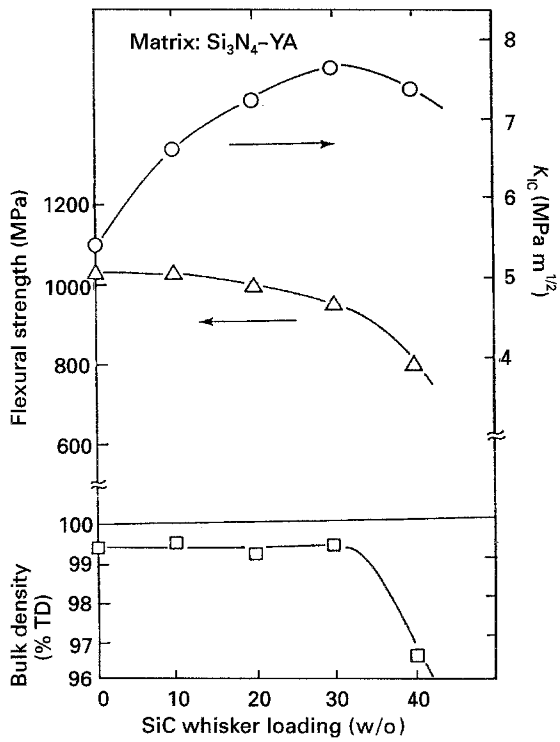

Figure 8 Effect of SiC whisker loading on flexural strength, fracture toughness and bulk density for Si_3N_4–SiC whisker composites.

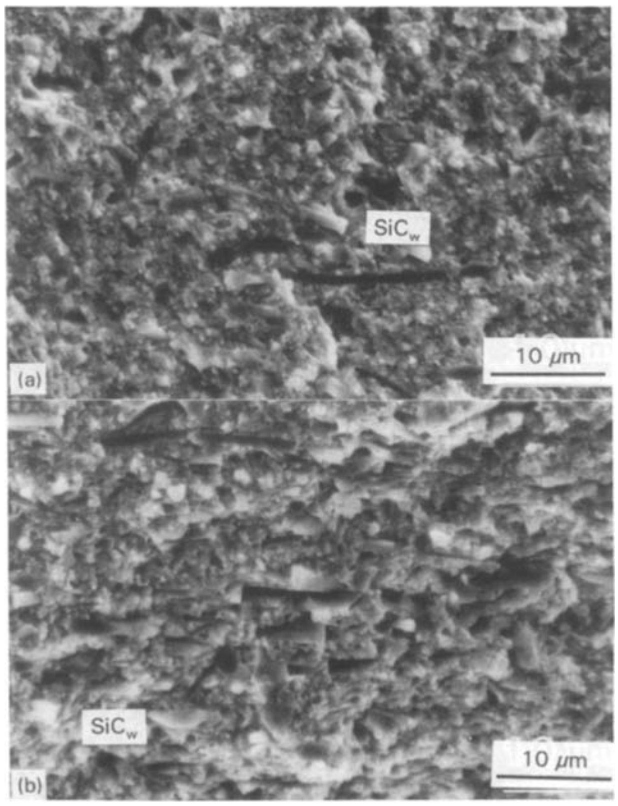

Figure 9 Scanning electron micrographs of fracture surface of Si_3N_4–20 wt % SiC_w composites. (a) YA matrix, and (b) YZ matrix.

3.2.2. Density and Mechanical properties

Fig. 8 shows the effect of SiC_w content on the density, flexural strength and fracture toughness, K_{IC}, of the composites with matrix (sintering aids system) YA.

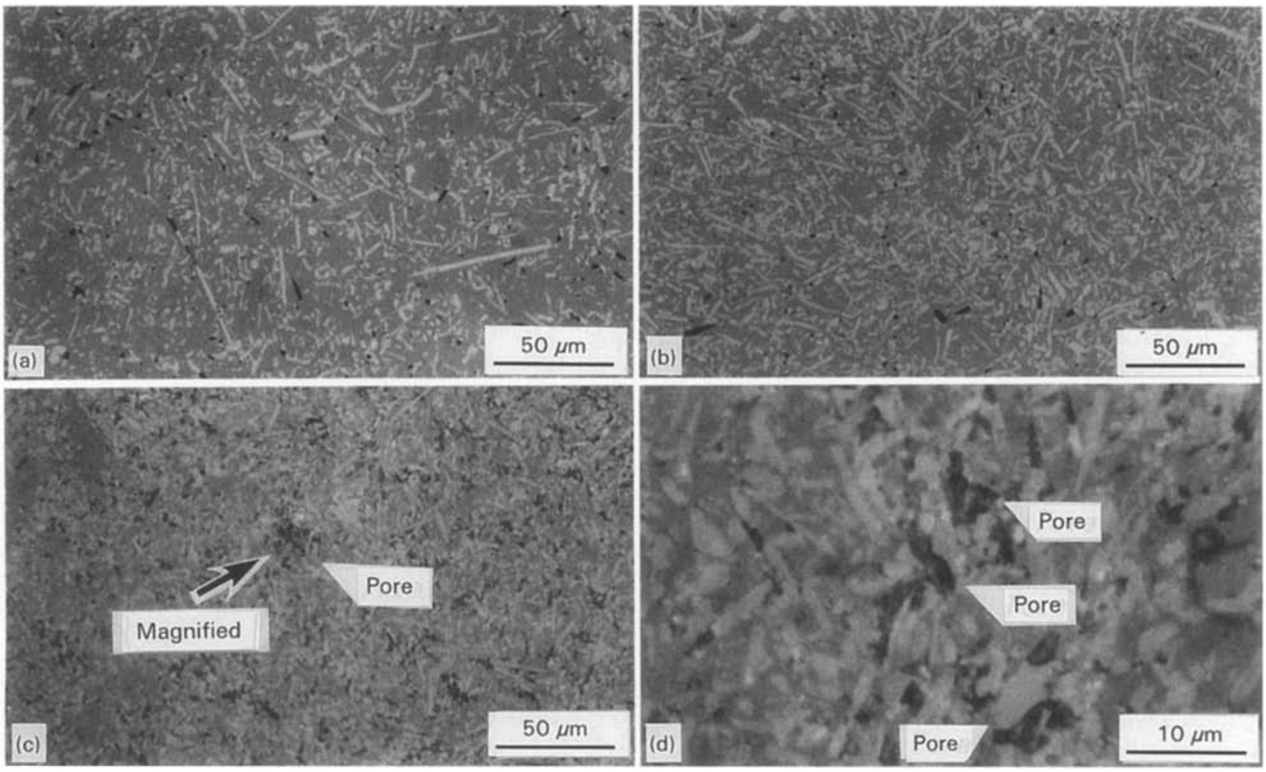

Figure 10 Optical micrographs of Si_3N_4–(20–40) wt % SiC_w composites: (a) 20 wt % SiC_w, (b) 30 wt % SiC_w, (c) 40 wt % SiC_w, and (d) magnified portion in (c).

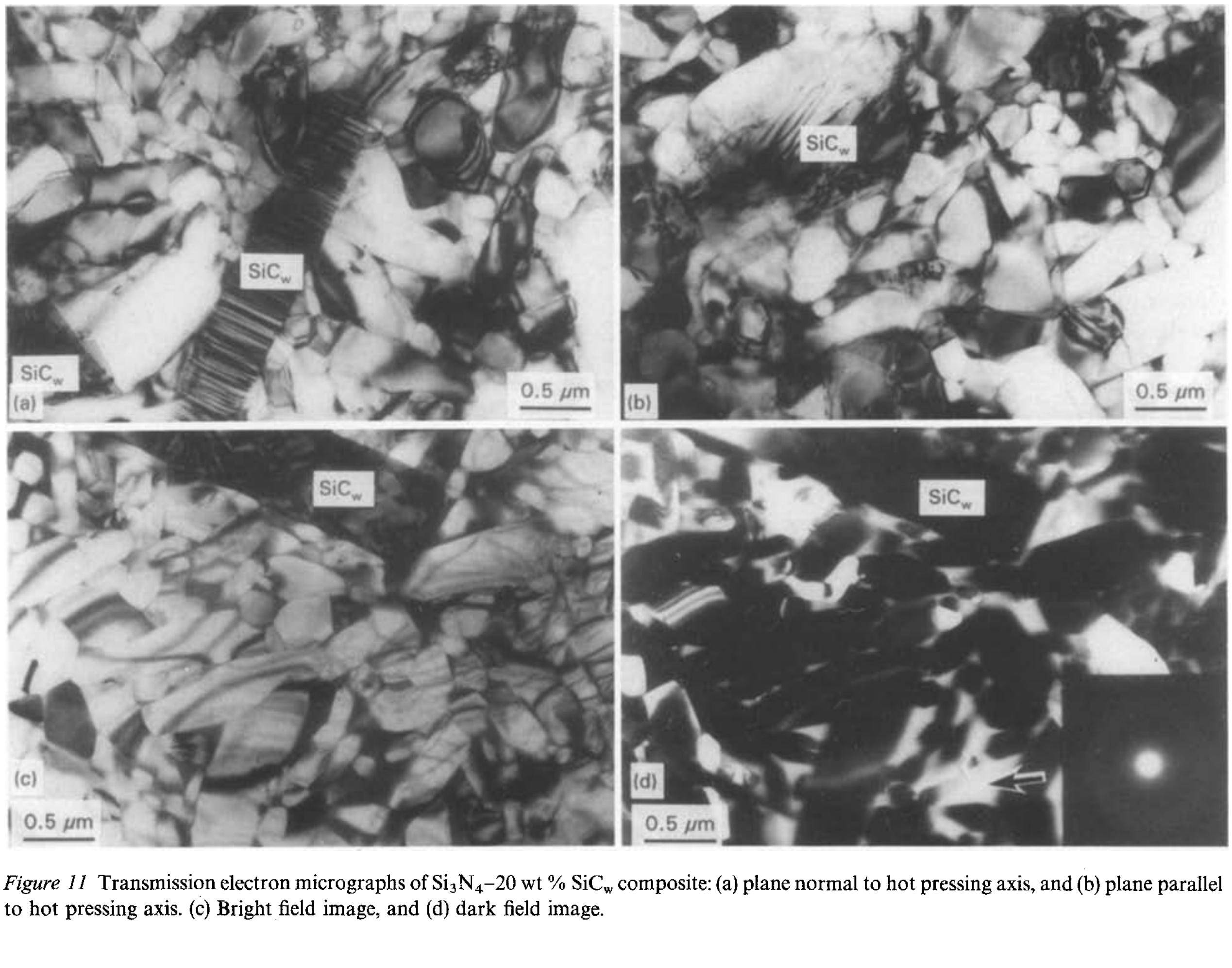

Figure 11 Transmission electron micrographs of Si_3N_4–20 wt % SiC_w composite: (a) plane normal to hot pressing axis, and (b) plane parallel to hot pressing axis. (c) Bright field image, and (d) dark field image.

A high density in excess of 99% theoretical density (TD) was achieved up to 30 wt % SiC_w content. The decrement of flexural strength was quite small, with increasing SiC_w content up to a maximum of 7.7 MPa $m^{1/2}$ at 30 wt % SiC_w. However, at 40 wt % SiC_w, the density reduced to 96.5% TD, and both flexural strength and fracture toughness decreased.

The fracture surfaces of the composites after K_{IC} measurement are shown in Fig. 9. Fig. 9a shows YA matrix, including 20 wt % SiC_w, and Fig. 9b shows matrix YZ, including 20 wt % SiC_w. Although the flexural strength of YZ was lower than that of YA, the fracture toughness of YZ was much higher than YA. Traces of whisker bridges and the whiskers (pull-out) themselves were not observed clearly in YA. On the other hand, they were observed clearly in YZ. The fracture surface of YA was rather flat compared to that of YZ. From this evidence, it was considered that the bonding strength of the interface between Si_3N_4 grains and SiC_w was lower in YZ than in YA.

3.2.3. Microstructure

Optical micrographs of Si_3N_4–SiC_w composite are shown in Fig. 10. At both 20 and 30 wt % SiC_w composites, whiskers are dispersed homogeneously. However, 40 wt % SiC_w composite shows some agglomeration of whiskers. When this area is magnified, some pores surrounded by whiskers are apparent. For the present experiment, since whiskers were incorporated without grinding, the aspect ratio of the whiskers was not changed from the as-received state. Therefore, it is considered that whiskers contacted and entangled each other, and densification was inhibited for 40 wt % whiskers loading.

Fig. 11a–d shows TEM micrographs of the 20 wt % SiC_w composite (YA). The whisker is oriented perpendicular to the hot pressing axis. The formation of acicular Si_3N_4 grain was little observed. Fig. 11c and d show the same TEM image by both bright and dark fields, respectively. The diffraction pattern attached to the dark field image shows a halo at the grain boundary. Therefore, there are glassy interphases between the Si_3N_4 grain and SiC_w.

4. Conclusions

1. Utilizing a two step pH adjustment of aqueous slurry, homogeneous dispersion of whiskers in the Si_3N_4–SiC_w system was achieved.

2. Through careful investigation of the correlation of slurry pH with zeta potential and viscosity, the pH for the slurry with good dispersion (pH 11) was fixed by changing pH to 7 where the slurry became extremely viscous and inhibited relative motion of the whisker against the powder.

3. In the sintered (hot pressed) body, fracture toughness was improved with whisker addition by 30 to 40%. Degradation of flexural strength with whisker addition was minimized by the newly developed process.

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