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# $Al_2O_3/ZrO_2$복합체의 기계적 물성 및 파괴거동

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# Mechanical Properties and Failure Analysis of $Al_2O_3/ZrO_2$ Composites

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**초 록** $Al_2O_3/ZrO_2$복합분말에 상용분말을 첨가하여 상압소결법으로 $Al_2O_3/ZrO_2$복합체를 제조한 후, 밀도, 강도, 경도 및 파괴인성등의 물성을 측정하였으며 미세구조 및 파괴단면도 관찰하였다. 상용분말의 첨가량이 중량비로 50%이하인 경우에는 평균 꺽임 강도가 640 MPa정도로 거의 변화가 없었으며, 50%이상 첨가된 경우에는 강도가 저하되었는데, 이는 미세조직과 관계가 있는 것으로 생각된다. 또한 파괴인성(4.3-5.3 $Mpam^{1/2}$)값은 상용분말 첨가량에 비례하여 증가하였다. 파괴단면 관찰결과 파괴원인으로는 가공에서 생기는 표면 결함, $ZrO_2$ agglomeration에 의한 crack-like void 및 $Al_2O_3/ZrO_2$ nano복합체 분말과 상용분말간의 소결성 차이에서 생기는 계면 분리등이 관찰되었는데, nano 복합 분말만을 사용한 소결체에서는 가공에 의한 표면 결함만이 파괴원으로 작용하였다. 또한, 파괴형태는 주로 transgranular fracture이었다.

***Abstract*** $Al_2O_3/ZrO_2$ *composites were fabricated by pressureless sintering from commercial powders and/or nano composite powder of* $Al_2O_3/ZrO_2$. *The properties of the composites such as density, strength, hardness and fracture toughness were evaluated. Microstructures and fracture surfaces were also examined.*

The flexural strength remains unchanged(~640 MPa) as long as the content of commercial powders is not extreamly high, and depends on microstructures of the composites. Fracture toughness(4.3-5.3$MPa \cdot m^{1/2}$) increases with increasing content of commercial powders.

Fractography shows that failure-initiating sources are 1)surface flaws resulting from machining damage, 2)crack-shaped voids formed due to $ZrO_2$ agglomeration, and 3)surface separation caused by inhomogeneous blending and by sinterability difference between nano composite powder and commercial powders of $Al_2O_3/ZrO_2$. Failure mode of the composites was mainly transgranular.

## I. Introuduction

Hot-pressing method has been mainly used to fabricate dense and fine grain ZTA($ZrO_2$-Toughened $Al_2O_3$) ceramics. Mechanical properties such as fracture toughness and strength have been reported in a number of papers, but *the relationship of mechanical properties and fracture behavior of ZTA ceramics fabricated from pressureless sintering*[1] *has been rarely studied.*

Since Engle and Hubner[2] initiated a systematic study relating strength to processing variables, Lange et al. [3-5] examined processing-related fracture origins of $Al_2O_3/ZrO_2$ composites and obtained the following results : Internal, crack-like surfaces responsible for the much-lower strength are located at the *fracture origins of sintered materials of* $Al_2O_3/ZrO_2$ *composite system, which are mainly pro-*

duced by the different sinterability of large agglomerates relative to their surroundings in the powder compact. The $ZrO_2$ agglomerates shrank away from consolidated $Al_2O_3/ZrO_2$ powder matrix during sintering and crack-like voids accounted for strength degradation.

Slurry/filtration route[6], CVD method[7], and sol-gel method[8-9] were investigated to preclude agglomeration of $ZrO_2$ powders and to fabricate $Al_2O_3/ZrO_2$ composites with uniform microstructures, but these methods have disadvantages such as complex and/or costly manufacturing processes.

This paper reports mechanical properties and failure analysis of $Al_2O_3$-15 vol% $ZrO_2$(+3 mol% $Y_2O_3$) composites fabricated from pressureles sintering, where commercial $Al_2O_3$ and Y-TZP powders were added to $Al_2O_3/ZrO_2$ nano composite powder prepared by co-precipitation method.

## Ⅱ. Experimental procedures

Materials used to prepare $Al_2O_3/ZrO_2$ system contains 15 vol% $ZrO_2$(+3 mol% $Y_2O_3$) in this study.

Tetragonal $ZrO_2$ is retained by the constraint of $Al_2O_3$ matrix and the addition of $Y_2O_3$ at sintering temperatures of $Al_2O_3/ZrO_2$ composites[10], and is a significant toughening agent.[11]

Nano composite powder of $Al_2O_3$-15 vol% $ZrO_2$(+3 mol% $Y_2O_3$) was prepared by co-precipitation of the common solution of $Al_2(SO_4)_3 \cdot 18H_2O$, $ZrOCl_2 \cdot 8H_2O$ and $YCl_3 \cdot 6H_2O$ with $NH_4OH$ at the pH=7, and followed by calcination of coprecipitated metal hydroxides at 1250 ℃ for 1hr.[12] The average particle size and specific surface area of the nano composite powder was 0.87㎛ and 15㎡/g, respectively.[12]

Transmission electron microscopy(TEM) was used for a more detailed observation of the powder microstructures, e.g., the morphology of $Al_2O_3$ particles and the dispersion state of $ZrO_2$ particles. Also, thin-foil energy dispersive X-ray spectroscopy(EDS) analysis using finely focused electron beams(~8 to 50nm) in TEM was employed to distinguish $Al_2O_3$ from $ZrO_2$ particles.

Composite powders for sintering were prepared by mixing the appropriate amounts of submicrometer-sized commercial $Al_2O_3$*, $ZrO_2$ (+3 mol% $Y_2O_3$)** powders and nano composite powder in alchol. The mixed composite powders were dried by rotary distillation. The mixtures were uniaxially(25 MPa) and isostatically presses(138 MPa) prior to sintering at 1650℃ for 2hr in air.

This sintered composties were cut into rectangular bars(3X6X33mm) for 3-point flexural test(cross head speed : 0.5mm/min, span : 2.54cm). All bar specimens were polished with diamond paste down to 1㎛ of roughness to preclude surface defects as much as possible.

Microstructures of the composites were examined in the back-scattered mode of the scanning electron microscope(SEM) after thermal etching at 1450℃ for 1hr. Failure mode and failure-initiating sources were observed on as-fractured surfaces in the secondary mode of SEM.

The values of fracture toughness were measured by the indentation method using the following equation.[13]

$$\frac{K_{IC}}{Ha^{1/2}} = 0.203(C/a)^{-3/2}$$

Where H is the hardness, a the impression radius and C the radial/median crack length.

## Ⅲ. Results and Discussion

Figure 1 shows morphology of $Al_2O_3/ZrO_2$ nano composite powder observed by high resolution TEM. $ZrO_2$ particles with 25-50nm sizes are homogeneously dispersed at the inner and outer parts of $Al_2O_3$ particles. $ZrO_2$ parti-

* Alcoa A-16, Aluminum Company of America, Pittasburgh, PA.
** HSY-3.0, Daichi-Kigenso, Tokyo, Japan.(Average particle size : p.5㎛)

Table I. Properties of $Al_2O_3/ZrO_2$ Composites

| Material | Content of Commercial Powders*(wt.%) | Sintered Density (% theoretical)** | Flexural Strength (MPa) | Hardness (GPa) | Fracture Toughness (MPa $m^{1/2}$) |
|---|---|---|---|---|---|
| ZTA0 | 0 | 97.5 | 637±30 | 10.9±0.5 | 4.3±0.7 |
| ZTA10 | 10 | 97.7 | 640±20 | 10.0±0.7 | 4.8±0.6 |
| ZTA30 | 30 | 98.0 | 630±25 | 11.3±0.9 | 4.8±1.0 |
| ZTA50 | 50 | 98.8 | 641±30 | 12.6±0.8 | 5.2±0.8 |
| ZTA80 | 80 | 99.0 | 530±50 | 12.9±0.8 | 5.3±0.8 |

* Composition of commercial powders : $Al_2O_3-15$ vol% $ZrO_2(+3$ mol% $Y_2O_3)$

** $\rho Al_2O_3=3.98g/cm^3$, $\rho ZrO_2=6.08g/cm^3$

# In all composites, tetragonal $ZrO_2$ was retained above 95% after polishing.

## In all composites, tetragonal $ZrO_2$ was retained in the range of 75-80% after fracture.

cles existing in inside of $Al_2O_3$ particles are lens shape. It may be considered that the former and the latter are under equiaxial and anisotropic compressive stress of $Al_2O_3$ particles, respectively.

Table I shows properties of $Al_2O_3/ZrO_2$ composites. The densities of the composites were more than 97% of theoretical density. The more the content of commercial powders increases, the higher the densities become. Lange and Hirlinger[14] reported that $Al_2O_3/ZrO_2$ interfacial energy is lower than $Al_2O_3$ grain boundary energy, which suggests that the formation of $Al_2O_3/ZrO_2$ interfaces would increase the driving force for densification. Also, Kibbel and Heuer[15] have that intergranular $ZrO_2$ particles grow faster than intragranular particles does, despite their initially larger size ; the kinetics of particle growth are clearly faster on the grain boundaries than within $Al_2O_3$ grains.

As shown in Figure 1, the increased content of $Al_2O_3/ZrO_2$ nano composite powder increases the number of $Al_2O_3/ZrO_2$ interfaces and intragranular $ZrO_2$ particles(smaller than intergranular and commercial $ZrO_2$ particles). Thus, with increassing the content of commercial powders, high density of the composites is shifted toward higher fractions under the same sintering condition.

The flexural strength remains unchanged(~640MPa) as long as the content of commercial powders is not extreamly high, and depends on microstructures of the composites. The effects of microstructures on strength can be explained in Figure 2. At the extreamly high content of commercial powders shown on Figure 2 (B), the $ZrO_2$ particles(white) was ineffective in pinning the $Al_2O_3$ readily occurred. At the lower weight fractions, shown in Figure 2(A), the $ZrO_2$ particles are uniformly located at the $Al_2O_3$ grain boundaries, effectively limiting the $Al_2O_3$ grain size. Therefore, even though the starting powders are the same composition, there must be difference in $ZrO_2$ particle-limited grain growth occurred during sintering, depending on starting powders.

Table I shows close relationship between hardness and density, where higher hardness was accompained by density increase.

Fracture toughness increases with increasing content of commercial powders. It can be explained by Figure 3 showing microcracking of the composites around indentation crack. At the higher weight fractions, such as shown on Figure 3(B), large $ZrO_2$ particles remain at the $Al_2O_3$ grain boundaries and they effectively absorb crack propagation energy by stress-induced phase transformation or crack deflection. At the lower weight fractions, small $ZrO_2$

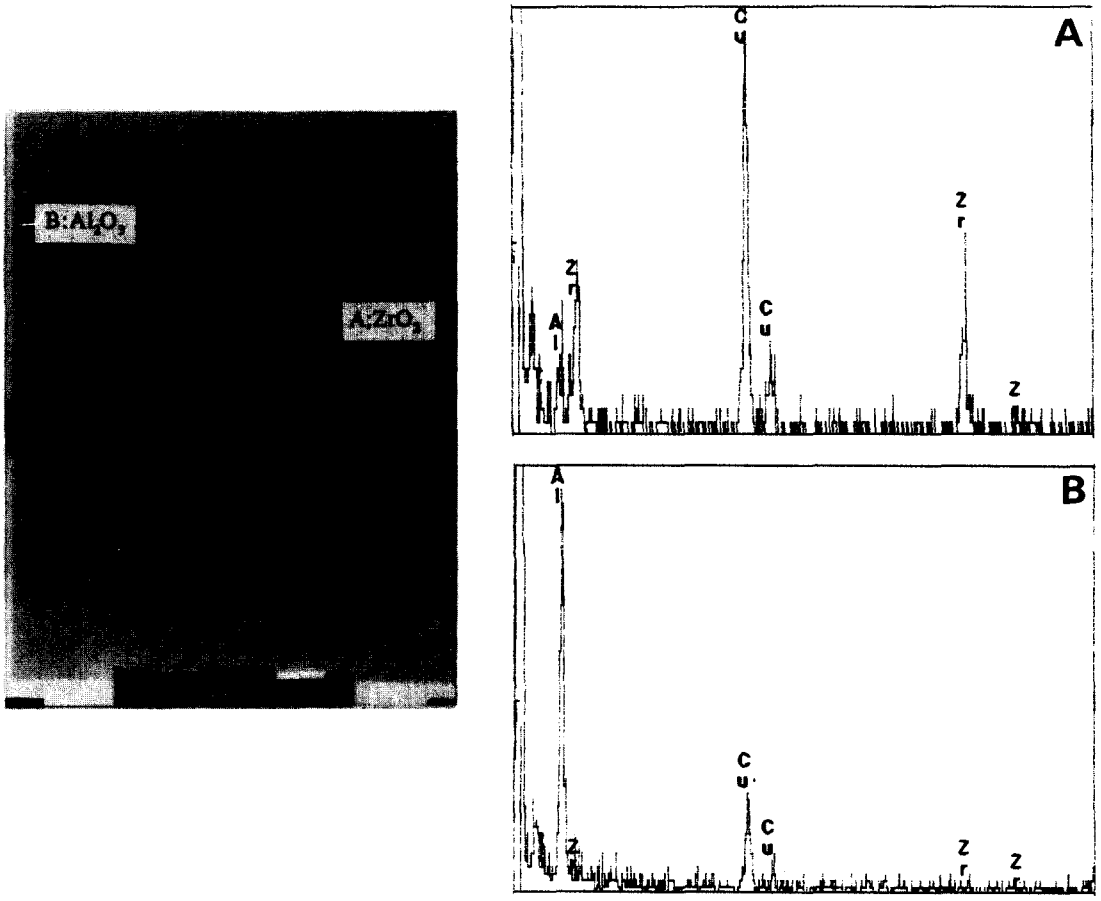


Fig. 1. Transmission electron micrograph and energy dispersive X-ray spectra $Al_2O_3/ZrO_2$ nano composite powder. [Cu detected due to copper grid]

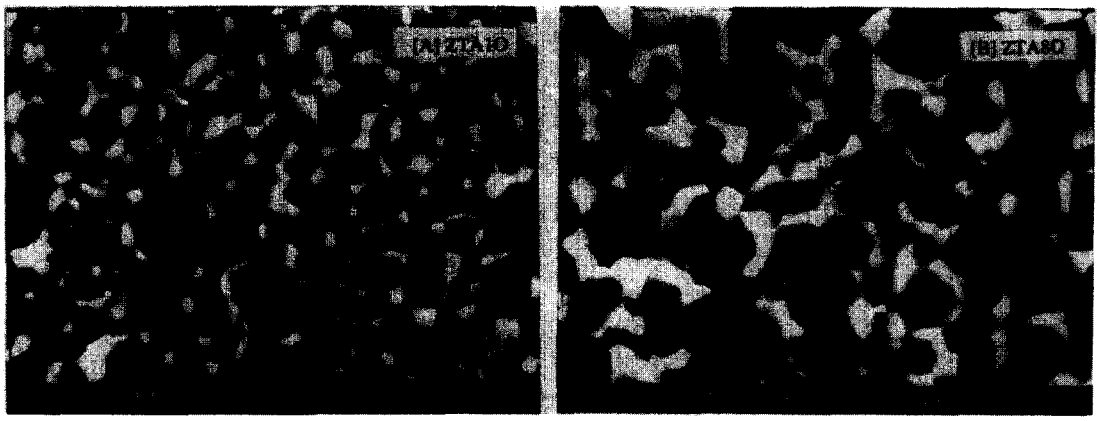

Fig. 2. The back-scattered scanning electron micrographs showing microstructures of $Al_2O_3/ZrO_2$ composites.

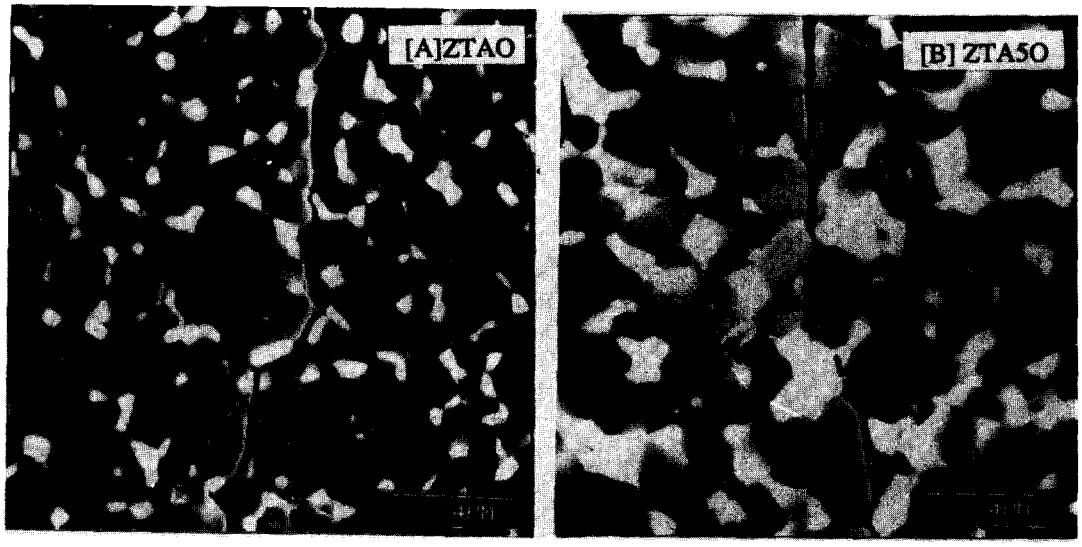


Fig. 3. The back-scattered scanning electron micrograph showing microstructures of $Al_2O_3/ZrO_2$ composites around indentation crack.

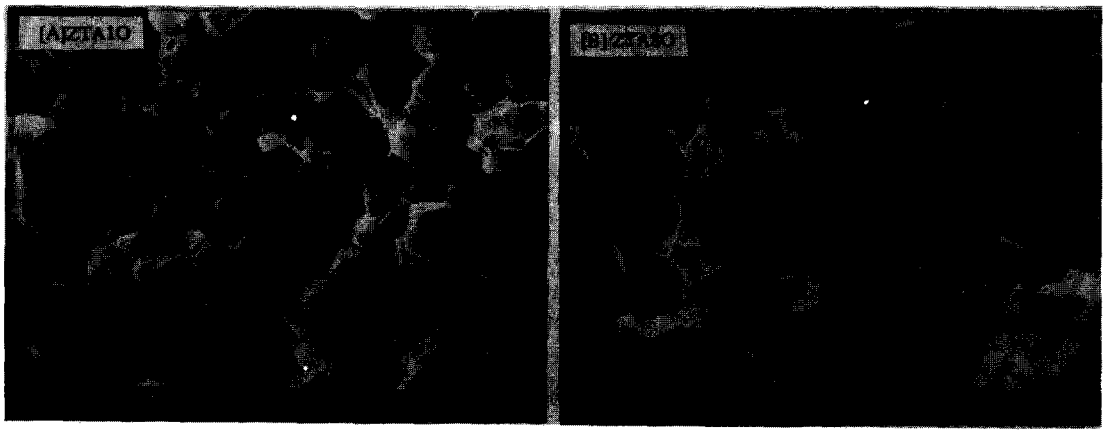


Fig. 4. Scanning electron micrographs of fracture surfaces of $Al_2O_3/ZrO_2$ nano composites.

particles are located at the $Al_2O_3$ grain boundaries, and only small fraction of $ZrO_2$ absorbs crack propagation energy. In all composites, $Al_2O_3$ grains showed a transgranular crack produced by a Vickers indenter.

Figure 4 shows the fracture surfaces of the composites. The fracture mode is mainly transgranular, and it agrees with the result observed in Figure 3. Figure 5 to 7 show failure sources of the composites observed in this

study. In the composite prepared from $Al_2O_3/ZrO_2$ nano composite powder alone, the fracture initiates from surface flaws created by machining damage on tensile surface(Figure 5). In the cases of adding commercial powders to $Al_2O_3/ZrO_2$ nano composite powder, crack-shaped voids formed due to $ZrO_2$ agglomeration and surface separation caused by inhomogeneous mixing and by sinterability difference between $Al_2O_3/ZrO_2$ nano composite powder and commercial powders as well as surface flaws are observed, and these act as factors of strength degradation(Figure 6). Especially, Figure 7 illustrates the morphology of a less-typical failure source and a matching hole was observed on the other side of the

Fig. 5. Scanning electron micrograph of a fracture origin of ZTAO.

fractured surface. Because of $Al_2O_3$ and $ZrO_2$ existing together, failure source is not formed due to $ZrO_2$ agglomeration like Figure 6. Also, in contrast to the fracture mode of Figure 4, the fracture mode within the hole(failure source) is intergranular.

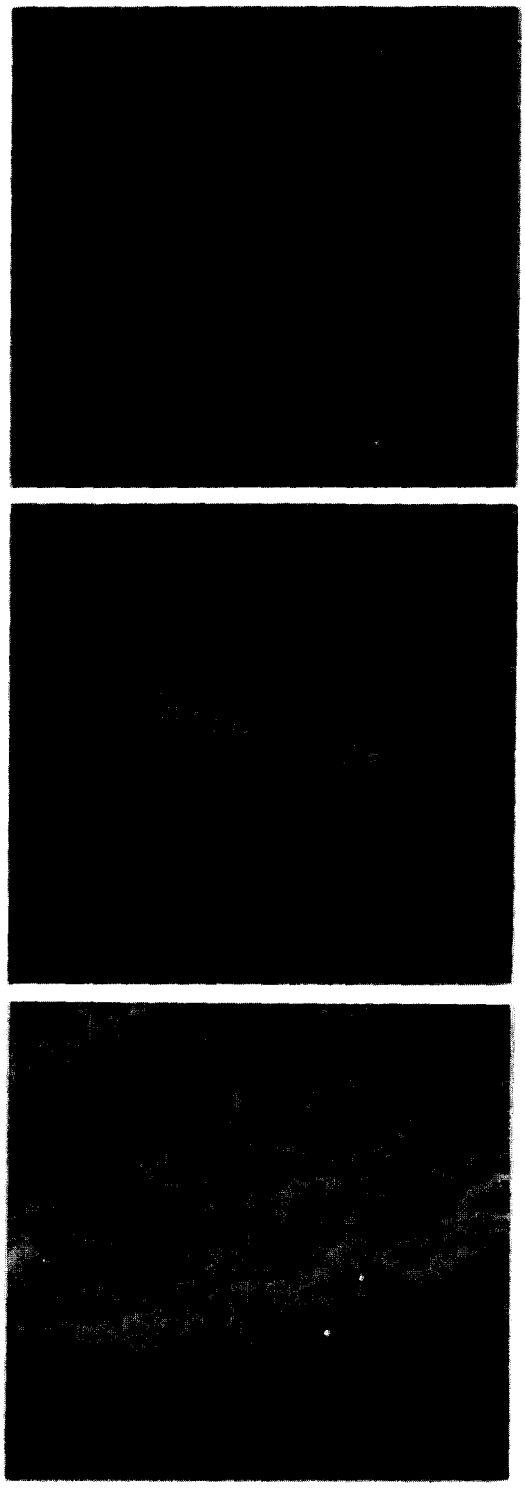

Fig. 6. Scanning electron micrograph of a fracture origin of ZTA30 with different magnitude.

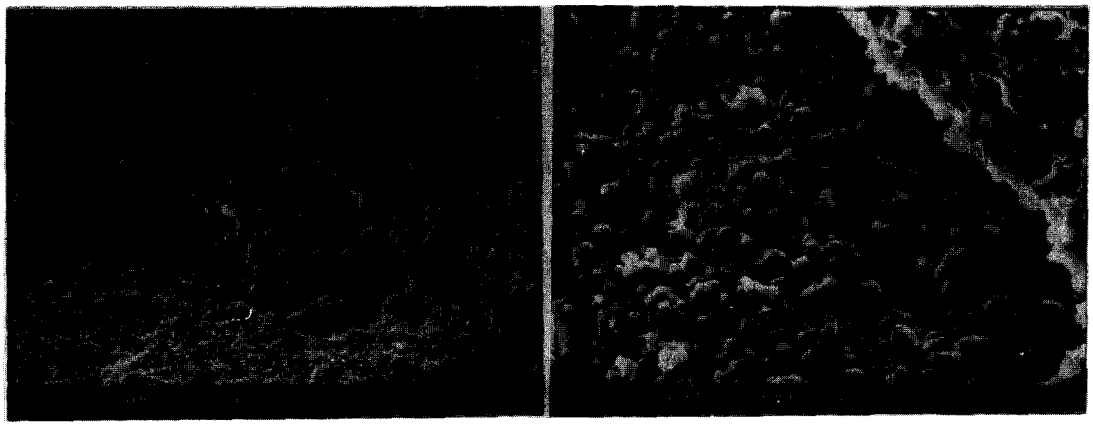

Fig. 7. Scanning electron micrograph of a fracture origin of ZTA80 with different magnitude.

## Ⅳ. Summary

The flexural strength remains unchanged(~ 640 MPa) as long as the content of commercial powders is not extreamly high, and depends on microstructures of the composites. Fracture toughness(4.3-5.3MPa · $m^{1/2}$) increases with increasing content of commercial powders.

Fractography showed that failure-initiating sources in $Al_2O_3/ZrO_2$ composites are surface flaws, crack-shaped voids and surface separation. Fracture mode of the composites are also mainly transgranular.

Crack-shaped voids and surface separation are not observed in the composite fabricated from $Al_2O_3/ZrO_2$ nano composite powder alone. Thus, it is considered that it can used as a reliable high-tech $Al_2O_3/ZrO_2$ composite, if its sinterability is somewhat improved.

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