# PHASE TRANSFORMATION CHARACTERISTICS OF NANO-SIZED ZIRCONIA-ALUMINA COMPOSITE POWDER

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## ABSTRACT

A series of highly homogeneous $ZrO_2$-$Al_2O_3$ composite powder was prepared by the spray-drying and calcination of mixed oxalate solution with any desired component ratio. The homogeneity extent(the separation range between $ZrO_2$ and $Al_2O_3$) is below 10Å as determined experimentally. The homogeneous mixing between $ZrO_2$-$Al_2O_3$ leads to a postponed crystallization of the tetragonal zirconia phase from amorphous phase at elevated temperatures. The grain growth of zirconia is greatly restrained by $Al_2O_3$ present in the composite powder as soon as $ZrO_2$ particles appear as an isolated phase surrounded by $Al_2O_3$ matrix. For pure zirconia, 50mol%alumina doped and 80mol%alumina doped composite powders calcined at 1000°C-25min the average grain sizes are 100nm, 30nm and 13nm(by XRD-Line Broadening) respectively. In the mean time, with grain growth restraining, the phase transformation of zirconia particles from tetragonal to monoclinic is obviously repressed by the $Al_2O_3$ surroundings. Higher temperature and larger critical grain size are needed for the phase transformation of composite powders with higher $Al_2O_3$ contents. For pure zirconia powder calcined at 800°C, the monoclinic content is higher than 95%(its critical grain size of transformation is equal to about 30nm at 600 C); but the monoclinic content of 80mol%alumina doped composite powder is less than 5% at 1300°C and 35% at 1550°C-3h.

## INTRODUCTION

The phase transformation characteristics of $ZrO_2$ materials are frequently stressed as the source of the socalled phase transformation toughening of ceramic materials[1,2]. The phase transformation behavior of zirconia is influenced by its particle size, dopant level and the external environmental condition like the restraints from a second phase[3,6]. The doping of a solid solute like $Y_2O_3$ can stabilize the tetragonal and cubic phases at room temperature[3]. For undoped zirconia powder, if a critical grain size is reached, tetragonal $ZrO_2$ will be stable at room temperature[3,5], but if the critical size is exceeded, the phase transformation from tetragonal to monoclinic will take place because of the decrease of the specific surface energy difference with the increase of particle size. The constraint from the second phase like $Al_2O_3$, etc. on $ZrO_2$ particles can alter the phase transformation behavior[6,7].

The effect of the second phase on the phase formation is greatly affected by the state of mixing of zirconia particles and the second phase, i.e. the powder processing[6]. In this paper, a new method of $Al_2O_3$-$ZrO_2$ composite powder preparation was developed resulting in the highly homogeneous mixing of the two components, and the phase transformation characteristics of zirconia particles in the composite powders under the constraint of alumina phase were studied.

## MATERIALS AND METHODS

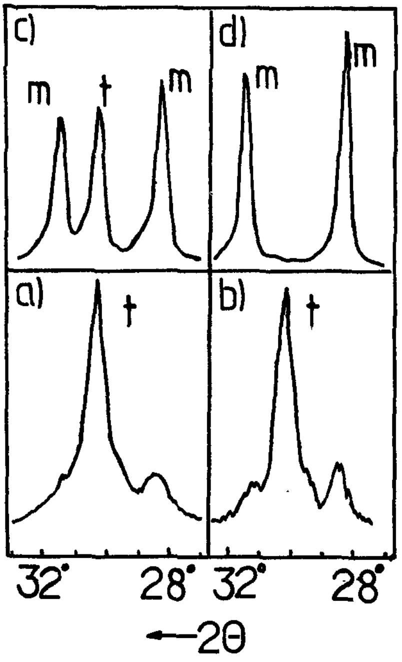
The oxalate solution of aluminum(27.4mg/ml) and zirconium(20.68mg/ml) were prepared in advance by the solution of their hydroxide in excess oxalic acid(A.R., Beijing Chemical Factory). The two kinds of complex solutions were mixed according to the desired mol content of $ZrO_2$ and $Al_2O_3$. The mixed complex solution was spray-dried in a mini-spray-dryer(Brinkmann/Buchi 190, Westbury, NY) and followed by the calcination at various temperatures for 25min to obtain the composite oxide powders. The decomposed powders are subjected to the XRD(Rigaku Denki Co.Ltd, RAX-10),TEM(JEOL Co., JEM-200CX) analysis.

## RESULTS

### 1, Phase Transformation Behavior of the Composite Powder by XRD

The XRD spectra of the powder containing only $ZrO_2$ by the decomposition of the spray-dried oxalate precursor at different temperatures are shown in Fig.1. It can be seen that at relative low temperature( $\leq 600^\circ C$), the main phase is metastable tetragonal, at 600°C monoclinic phase starts to occur and its content increase with the increase of temperature. At 800°C, the tetragonal phase no longer exists in the powder. The phase transformation behavior of the pure $ZrO_2$ powder is similar to that prepared by the decomposition of other salts[8].

The presence of $Al_2O_3$ in the powders results in a considerable change of the zirconia phase transformation behavior, which means the increasing stability of the metastable tetragonal phase. In a previous report by Murase et al.,the effect of $Al_2O_3$ phase on the phase transformation behavior has not been fully brought to play becasuse of the inhomogeneous mixing of the two components. As the composite



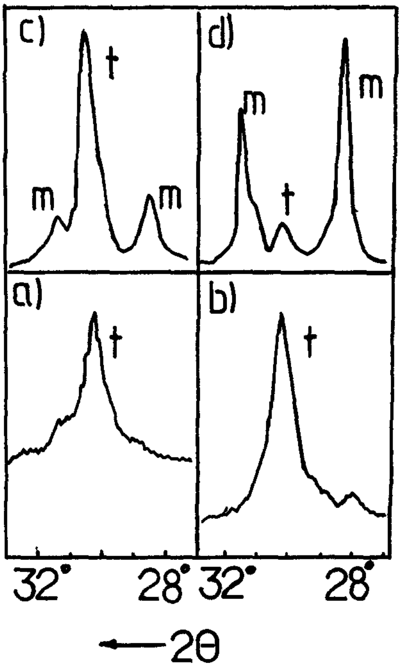


Figure 1. XRD Spectra of Pure ZrO2 Powder at (a)400°C, (b)500°C, (c)600°C and (d)800°C(Left)

Figure 2. XRD Spectra of 20mol%Alumina-Zirconia Powder at (a)420°C, (b)650°C, (c)800°C, (d)1000°C(Right).

powders in our experiments were obtained from the thorough mixing the complex solutions, the presence of Al2O3 affected ont only the stability of the metastable tetragonal phase, also the crystallization of the ZrO2 metastable tetragonal phase. Fig.2 shows the phase composition of a composite powder containing 20mol%Al2O3. Tetragonal ZrO2 began to crystallize out at about 420°C, and monoclinic phase occurred at 650° C. At 800°C, the content of monoclinic phase was only 26% while that of pure ZrO2 powder had reached 100% at 800°C as shown in Fig.1.

The phase transformation behavior of ZrO2 was further altered as the Al2O3 content in the composite powder increases. The metastable tetragonal phase crystallize out at about 800° C and the tetragonal phase could be maintained up to 1200 ° C, as can be seen in Fig.3, for the composite powder containing 50mol%Al2O3. So the adding of alumina into the composite powders postpones the crystallization of the tetragonal phase in one hand and restrains the phase transformation from tetragonal to monoclinic.

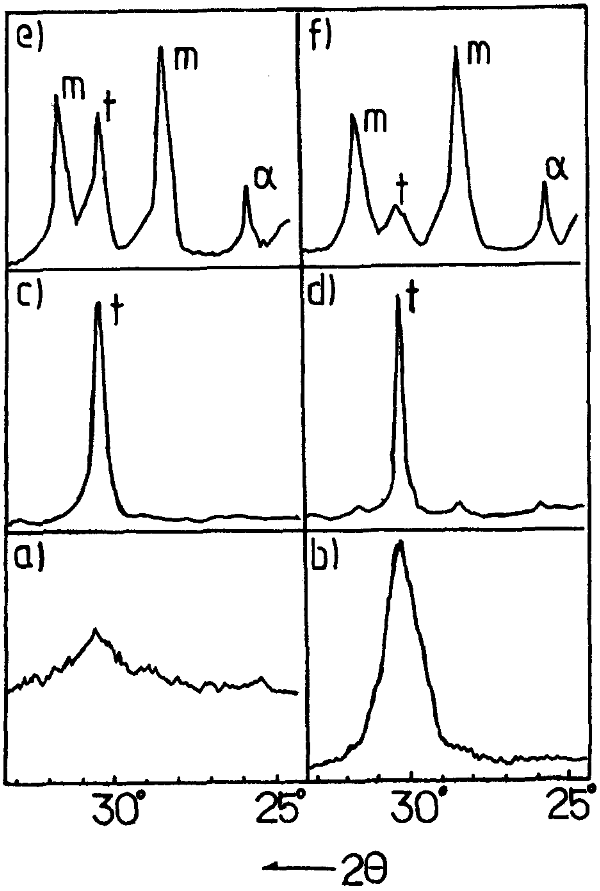


Figure 3. XRD Spectra of 50mol%Alumina-Zirconia Powder at (a)700°C, (b)800°C, (c)1000°C, (d)1200°C, (e)1420°C and (f)1500°C.

Fig.4 shows the temperature dependence of the phase composition of zirconia in the composite powders with different alumina contents. The effect of alumina content on the phase transformation behavior(expressed as the tetragonal content in the figure) of zirconia are clearly illustrated from the figure. For example, in the composite powder with 80mol%alumina, the tetragonal content still remains at 65% when calcined at 1550°C for 3h, and it reaches 76% for the composite powder containing 90mol%alumina at the same condition. Fig.5 is the XRD spectra of 80mol%alumina containing composite powder, the phase transformation behavior of zirconia in the composite powder is evidently shown. In addition, the diffraction peaks of a alumina can be seen in Fig.5 at 1000°C and beyond. The diffraction strength of alumina is relatively low in relation to its content, implying that the X-ray diffraction ability of the alumina crystal line

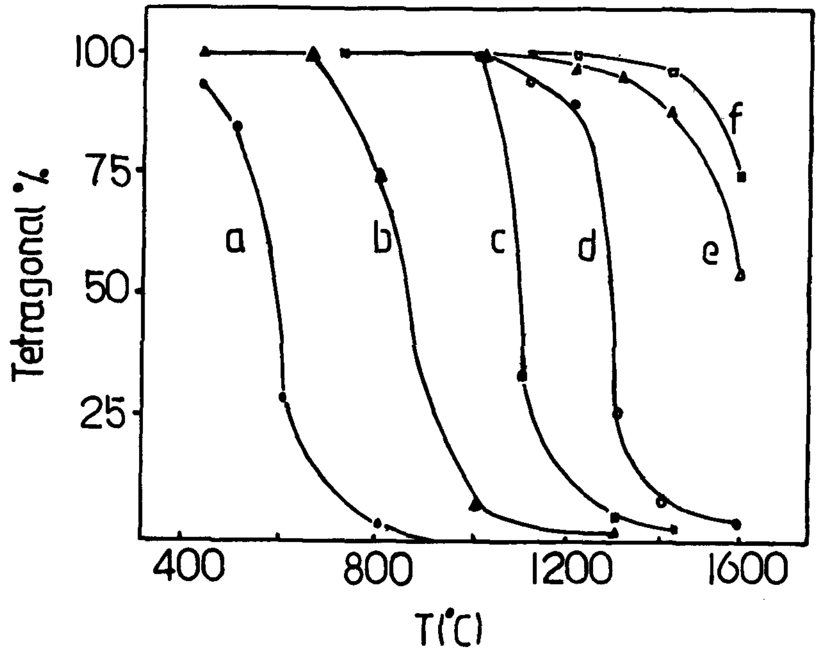


Figure 4. Content of Tetragonal Zirconia vs Alumina content, (a)Pure Zirconia, (b)20mol%Alumina, (c)35mol%, (d)50mol%, (e)80mol%, (f)90mol%.

faces(α-Al2O3) is much lower than that of zirconia(this inference is confirmed by the standard Al2O3-ZrO2 samples deliberately compounded).

### 2, Powder Morphology and the Phase Transformation

Particle morphologies of the composite powder containing 50mol%alumina at various temperatures are shown in Fig.6-9. At 500 °C, the spherical particles are very homogeneous and no contrast can be seen(figure 6(a)). The electron diffraction(Fig.6(b)) analysis shows the amorphous diffraction pattern, the same with the XRD analysis. Besides, the EDS analysis shows the mixed patterns of the characteristic X-ray strength of Zr and Al(Fig.6(c)), showing that the co-existence of alumina and zirconia in the diffraction range.

The particle morphology of 800°C calcined powder shown in Fig.7 illustrates the occurence of contrast within the spherical particles suggesting component separation, corresponding to the crystallization of the tetragonal phase as identified by XRD(Fig.3) and confirmed with the ED analysis in Fig.7(b). Calcination at higher temperature of

1000 °C only leads to a larger component separation range, as shown in Fig.8, but does not change the phase structure of zirconia and the spherical shape of the particles

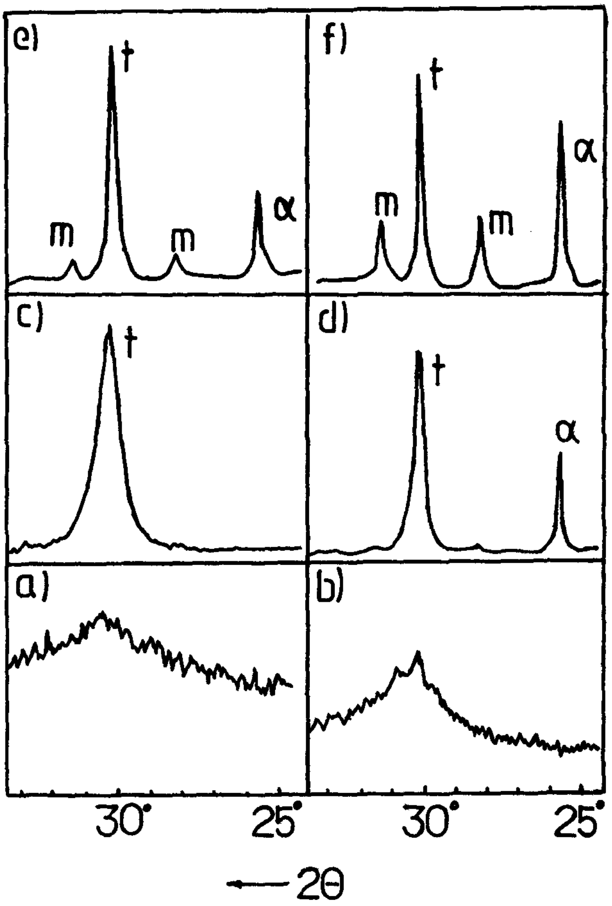


Figure 5. XRD Spectra of 80mol%Alumina-Zirconia Powder at(a)700C, (b)800 C, (c)1000C, (d)1200C, (e)1420C and (f)1550C

resulted from solution spray-drying.

Only about 10% tetragonal phase is left when the composite powder is calcined at 1350°C as shown in Fig.4. The phase transformation is accompanied by a distinct change of the particle morphology as illustrated by Fig.9---the previous existed spherical particles are no longer present in the composite powders. The ED analysis shows that the diffraction patterns of monoclinic ZrO2 and Al2O3 phase taken from regions A and B(Fig.9(b)) respectively. EDS analysis(Fig.9(c)) again shows that the region A and B are $ZrO_2$ and $Al_2O_3$ as illustrated. Since region A is darker in contrast than region B, so it is referred that ziconia component appears as isolated particle-like phase with darker contrast and alumina tends to be the continuous phase with less darker contrast(ref.Fig.7 and 8). The difference in contrast between alumina and zirconia is thought to be due to their different densities.

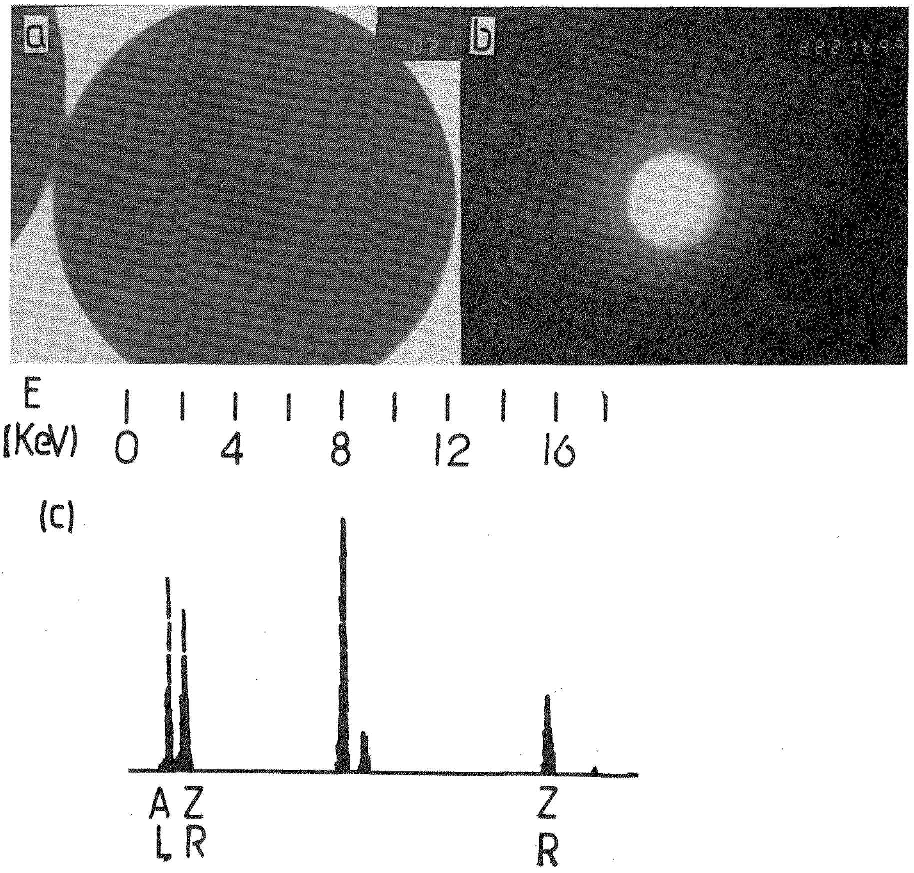


Figure 6. Powder Characteristics of 50mol%Alumina-Zirconia at 500°C, (a)Particle Morphology, (b)ED Pattern and (c)EDSspectrum

The phase transformation behavior of zirconia is largely dependent on the alumina content in the composite powders. Fig.10 shows the particle morphology of the composite powder containing 20mol%alumina which was calcined at 800° C. It can be seen that the spherical particles are broken at 800° C and zirconia particles appeared very obviously(compared to Fig.7) and ED pattern shows that the particles arepolycrystalline(Fig.10(b)). In contrast, 80mol% alumina added composite powder shows rather different particle morphology even at 1350 C, as can be seen in Fig.11. The

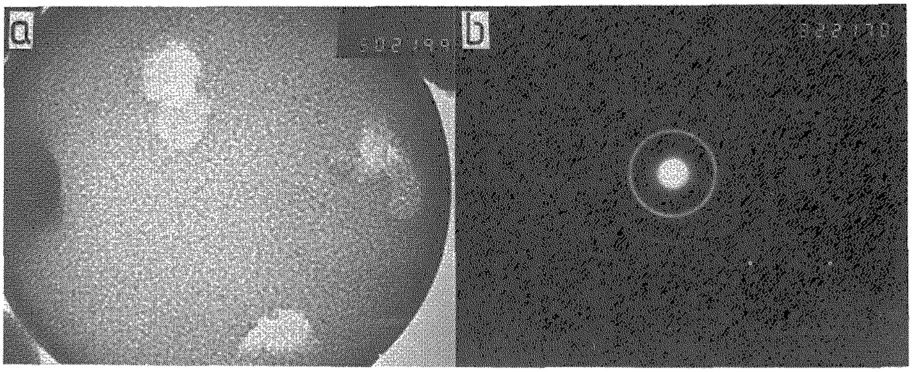


Figure 7. Powder Characteristics of 50mol%Alumina-Zirconia at 800°C, (a)Particle Morphology and (b)ED Pattern

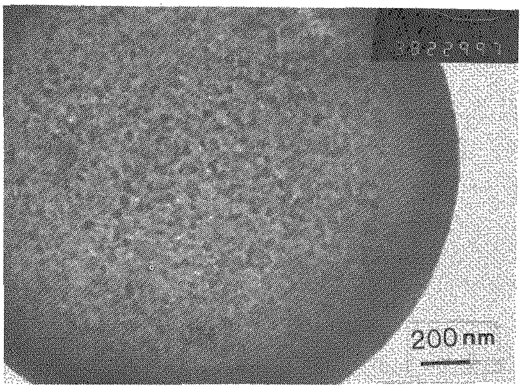


Figure 8. Particle Morphology of 50mol%Alumina-Zirconia at 1000°C

spherically shaped particles are still maintained even at 1350°C and isolated zirconia particles(darker areas in contrast) distribute homogeneously in the alumina surroundings. Such zirconia particles are tetragonal according to Fig.4.

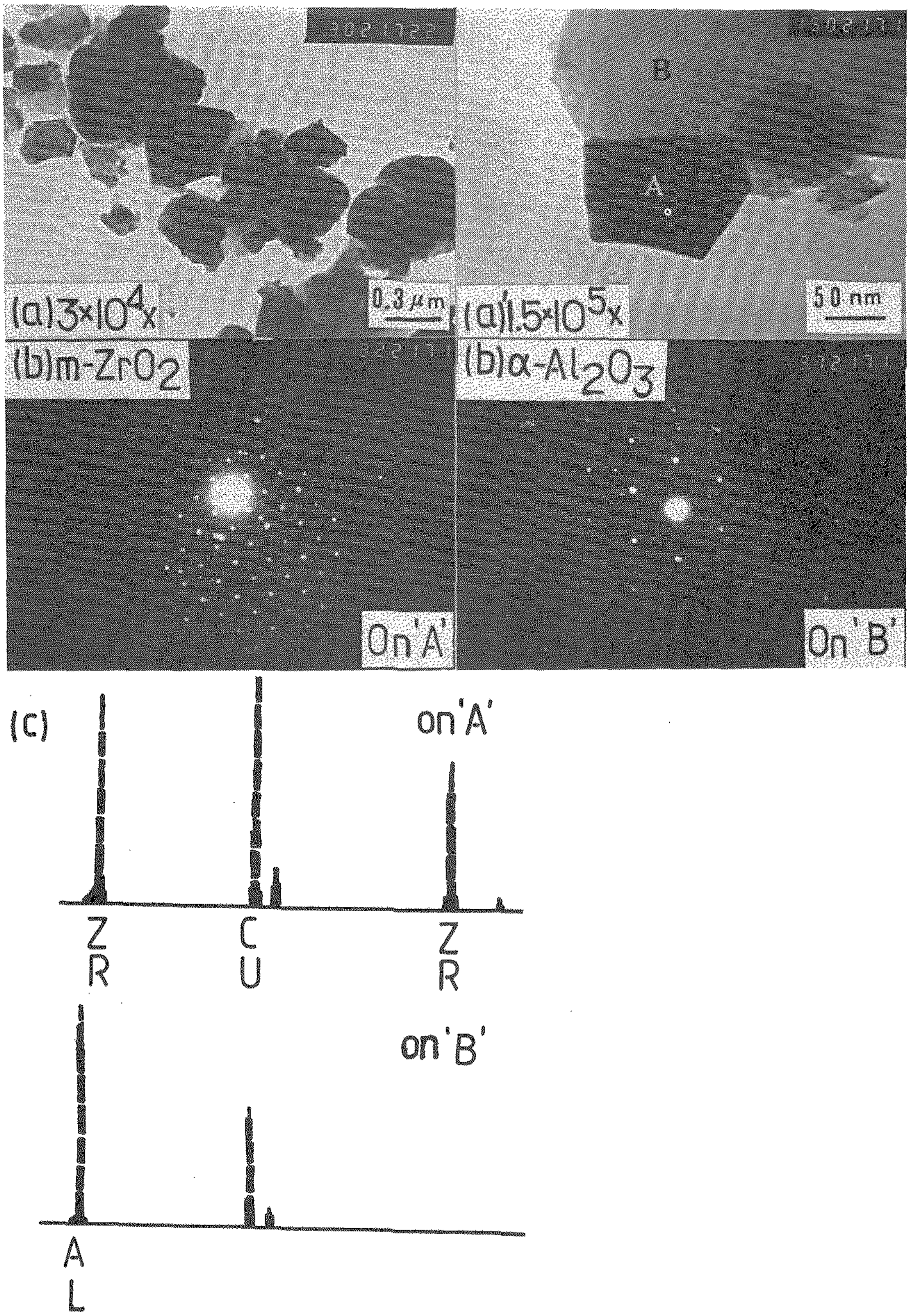


Figure 9. 50mol%Alumina-Zirconia Powder at 1350°C,(a)Particle Morphologies, (b)ED Patterns and(c)EDSspectra on Region A and B in (a)'

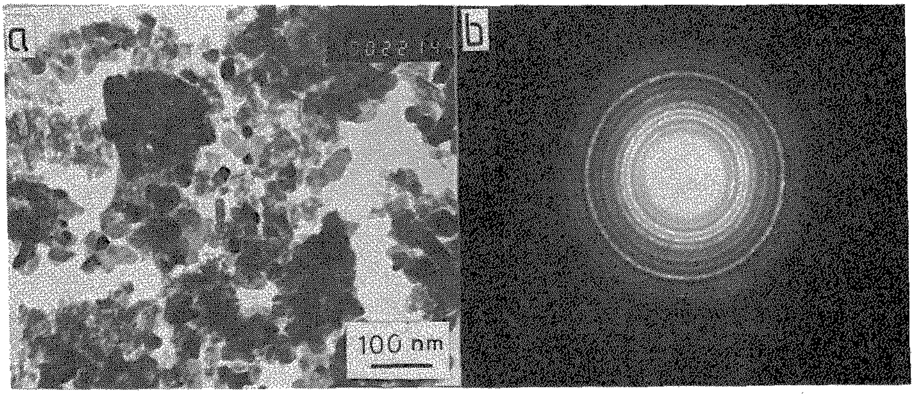


Figure 10. Powder Morphology(a) and ED Pattern(b) of 20mol%Alumina-Zirconia at 800°C

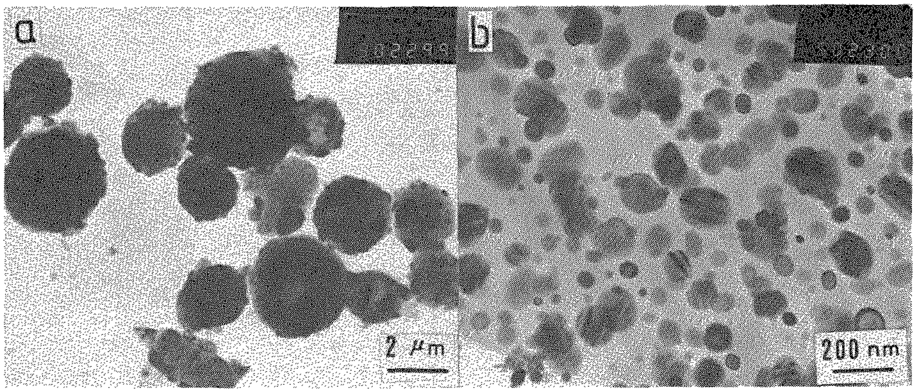


Figure 11. Powder Morphology of 80mol%Alumina-Zirconia at 1350°C, (a)5000× and (b)50000×

## DISCUSSION

### 1, The Initial Mixing Homogeneity and the Crystallization of Tetragonal Zirconia

Tetragonal zirconia crystallized at less than 400°C(Fig.1) in pure zirconia powder. The XRD Analysis shows that the composite powders tend to crystallize at higher temperatures when alumina was added into the powders, that is, the composite powders are amorphous at temperatures higher than the crystallization temperature of pure zirconia. Fig.12 shows the crystallization temperature of tetragonal zirconia in the composite powders vs alumina content(mol). The presence of alumina in the powders apparently raised the crystallization temperatures of tetragonal zirconia, The amorphous phase dominating in the composite powders containing alumina at higher temperature reffects the homogeneous mixing between alumina and zirconia. As the diffraction patterns of the amorphous powders always show one or more very scattered "peak", a "grain size" of about 20nm or so is estimated with the peak breadth at half height from Fig.3. Calcination at lower temperature would lead to wider "peaks" and smaller estimated size.

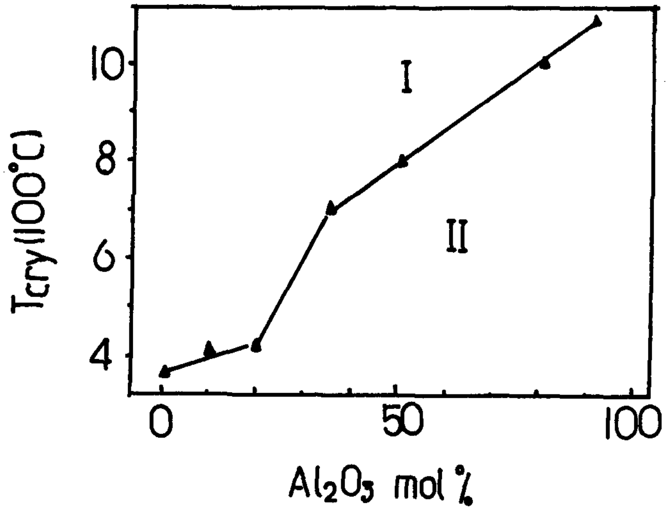


Figure 12. Crystallization Temperature of Tetragonal Zirconia vs Alumina Content in Composite Powders

A resolution of 10Å for the electron microscope(JEM-200CX) is easy to obtain. The TEM picture of some amorphous composite powders(e.g., Fig.6) shows no visible details by naked eyes(the possible size of the details in the figure is less than the resolution range of naked eyes--about 0.1mm). So the inhomogeneity range( the separation range of components) is smaller than 0.1mm/magnification. As the magnification in Fig.6(a) is 100000×, thus the inhomogeneity range in the amorphous composite powders is less than 10Å and at lower temperature the component separation range will be smaller. For other composite powders at the amorphous state, their inhomogeneity ranges are equally smaller than 10Å.

The homogeneous mixing between alumina and zirconia in the composite powders explains the postponed crystallization of tetragonal zirconia, which is so finely dispersed. Powders with higher alumina content need higher calcination temperature at which the ionic species of zirconia molecules are active enough to diffuse beyond the impedance of alumina and form a zirconia particle with a critical size for its crystallization.

## 2, Relation betweern Restraint, Particle Size and Phase Transformation from Tetragonal to Monoclinic

The homogeneous mixing between alumina and zirconia inhibits the formation of crystallized zirconia particles in the

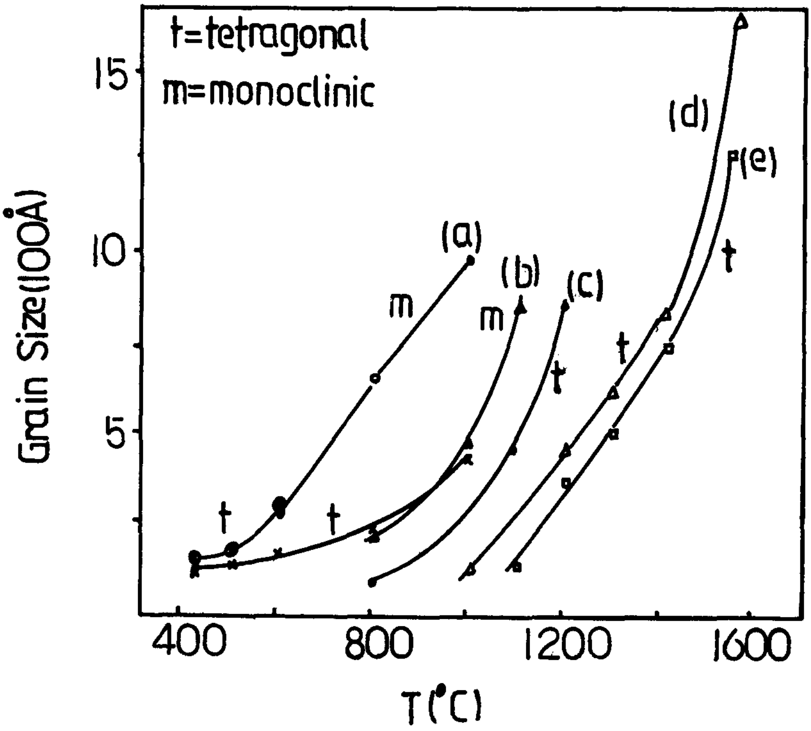


Figure 13. The Grain Growth of Tetragonal Zirconia in the Composite Powder, (a)10mOl%Alumina, (b)20mol%, (c)50mol%, (d)80mol% and (e)90mol%

surroundings of the continuous alumina phase. The surroundings no doubt will exert restraints(compresive force) on the zirconia particles as the particles grow. Such an effect is clearly shown in Fig.13.

It can be found from Fig.4 and 13, the restraint of alumina on zirconia particles inhibits the grain growth and increases the grain size at which the phase transformation from tetragonal to monoclinic may take place. With more alumina in the composite powder, the zirconia particles will be more highly dispersed,i.e. having longer separation distance. As discussed in the above point, higher temperature would be needed for the grain growth of zirconia particles when a stronger driving force for diffusion could be prevailing. At the same time, the alumina matrix material will be more densely sintered. It is known that the the phase transformation of t-ZrO2 to m-ZrO2 is accompanied by 3-5% linear expansion. Therefore, for composite powders with higher alumina content, tetragonal zirconia will be retained stable under such conditions of restraint. Furthermore, a larger grain(particle) size will be needed to allow such a phase transformation to occur. So the alumina component in the composite powders inhibits the grain growth of tetragonal zirconia and raise the critical size for the phase transfromation.

## CONCLUSIONS

In the initial homogeneously mixed composite Al2O3-ZrO2 powders, the crystallization temperature of ZrO2 is increased by the amount of alumina present and its restraining effect, The grain growth of zirconia in the composite powders is also inhibited to different degrees by the alumina restraint obviously. The phase transformation from tetragonal to monoclinic in the composite powder is retarded by the increasing of the critical size for the phase transformation to ouuur and the inhibiting effect on the grain growth of zirconia particles.

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