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Effect of mixing procedures and compaction pressures on the powder reaction of CuO–η-Al_2O_3 and ZnO–η-Al_2O_3 systems

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The rate of reaction of the compacted powders of CuO–η-Al_2O_3 and ZnO–η-Al_2O_3 systems was measured in air at 800 to 900° C and the effect of the mixing procedure (dry and wet mixing) and compaction pressure (0 to 8.3×10^8 Pa) of reactant oxides on the fraction of reaction completed (α) was investigated. In the reaction of the CuO–η-Al_2O_3 system, the α-values obtained for the sample prepared by wet mixing in ethanol were higher than those for the sample prepared by dry mixing in air and were not influenced by the compaction pressure, whereas in the case of dry mixing they varied with the compaction pressure and had a maximum value at 2.1×10^8 Pa. On the other hand, in the reaction of the ZnO–η-Al_2O_3 system the α-values for the sample obtained by wet mixing were lower than the values obtained by dry mixing, in contrast to the results in CuO–η-Al_2O_3 system, and the α-values for the samples prepared by both dry and wet mixing were not influenced by the compaction pressure. The effect of mixing procedure and compaction pressure of reactant powders on the α-values was found to be explained on the basis of the aggregate size of CuO and ZnO dispersed in the matrix of η-Al_2O_3 fine powder.

1. Introduction

The reactivity of solids, which is, in general, represented by the rate, the extent of reaction and the onset temperature of reaction, etc., is remarkably influenced not only by their structures and properties, but also by the conditions of mixing the reactant solids. In particular, in the powder reaction the contact state between reactant particles varies with particle size, shape, mixing procedure, mixing ratio and so on. Komatsu reported that the reaction rate in $CaCO_3$–MoO_3, CuCl–Si [1] and NiO–Al_2O_3 [2] powder systems which are mixed in various molar ratios can be explained on the basis of the idea of the number of contact points between spherical reactant particles of similar size. However, in the real powder systems the irregular aggregation of reactant particles often occurs so that it is impossible to apply the reaction model based on the idealized geometry to such a system. Although an investigation based on the real geometry of reactant particles is needed, very few authors have attempted to study microstructural features in correlation with the reaction mechanism of $ZnAl_2O_4$ formation [3, 4].

The purpose of present study is to investigate the effect of mixing procedures (dry and wet mixing) and compaction pressures of reactant oxides on the powder reaction of CuO–η-Al_2O_3 and ZnO–η-Al_2O_3 systems and to obtain information on the relationship between the fraction of reaction completed (α) and the aggregate size of CuO and ZnO dispersed in the matrix of the η-Al_2O_3 powder.

2. Experimental procedure

2.1. Materials

η-Al_2O_3 was prepared by the thermal decomposition of bayerite (β-$Al_2O_3 \cdot 3H_2O$) at 700° C for 3 h in air. Bayerite was obtained from a gel precipitated at 4 to 7° C by adding 250 ml 10 wt % $Al(NO_3)_3$ solution to 800 ml 4 M NH_4OH solution at a dropping speed of 3 to 6 ml min^{-1} and a constant stirring speed. After being left to age in the mother liquor (pH > 11) at 14° C for 24 h, the gel was filtered, washed and then dried in a vacuum oven at 45° C for 24 h. CuO and ZnO were prepared by the thermal decomposition of basic cupric carbonate, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ and basic zinc carbonate, $5ZnO \cdot 2CO_3 \cdot 4H_2O$ at 700° C for 1 h and at 500° C for 30 min in air, respectively. These powders of CuO or ZnO and η-Al_2O_3 were sieved to obtain − 300 mesh fraction and then mixed in an equimolar ratio using an agate mortar in air and in ethanol (in pasty state) for 1 h. All reagents used were GR grade from Kanto Chemical Co. Inc.

2.2. Reaction

The equimolar mixtures of CuO and η-Al_2O_3 (250 mg) and ZnO and η-Al_2O_3 (350 mg) were compacted to form a tablet 1 cm in diameter under pressures of 0, 0.9, 2.1, 4.1, 6.3 and 8.3×10^8 Pa. The tablet was divided into several pieces and then a piece 50 to 70 mg taken in a porcelain boat was heated in an electric furnace maintained at the desired temperature (800, 850 and 900° C) and for various times in air.

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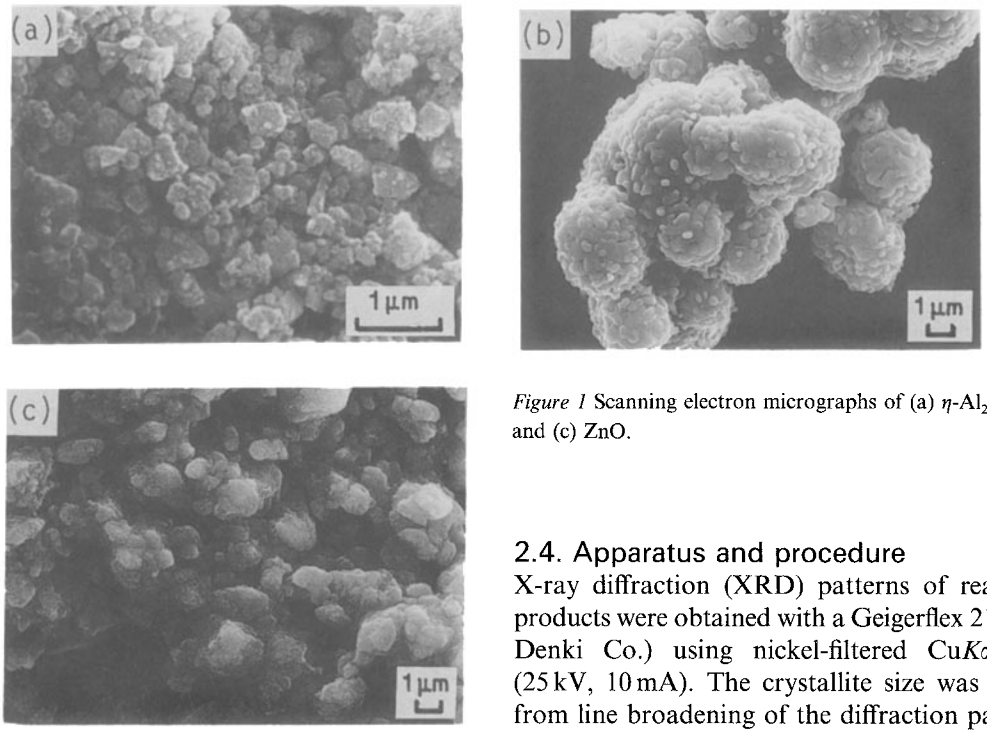

Figure 1 Scanning electron micrographs of (a) η-Al_2O_3, (b) CuO and (c) ZnO.

2.3. Chemical analysis of CuO and ZnO

The fraction of reaction completed (α) was estimated from the difference between the amounts of CuO or ZnO in the sample before and after the reaction. After the reaction the piece was ground in an agate mortar for 20 min. The unreacted CuO was extracted from the ground product by heating it in 50 ml NH_4OH–NH_4Cl solution (250 g NH_4Cl + 1 l NH_4OH + 2.5 l H_2O) in a flask equipped with a condenser, for 25 min. The undissolved residues (η-Al_2O_3 and $CuAl_2O_4$) were removed from the cooled extract by filtration, and the amount of Cu^{2+} ion in the filtrate was determined by titration with 0.01 M ethylene diamine tetracetic acid (EDTA) solution, PAN as indicator, triethanolamine as masking agent for the Al^{3+} ion and ethanol (10 ml) which makes the end-point sharp. The unreacted ZnO was extracted with 50 ml NH_4OH–NH_4Cl solution at room temperature for 10 min. The undissolved residues ($ZnAl_2O_4$ and η-Al_2O_3) were filtered from the cooled extract, and the amount of Zn^{2+} ions in the filtrate was determined using 0.01 M EDTA solution, Eriochrome Black (BT) as indicator and triethanolamine.

2.4. Apparatus and procedure

X-ray diffraction (XRD) patterns of reactants and products were obtained with a Geigerflex 2141 (Rigaku Denki Co.) using nickel-filtered Cu$K\alpha$ radiation (25 kV, 10 mA). The crystallite size was determined from line broadening of the diffraction pattern using an internal standard of 9 N silicon (−200 mesh).

Scanning electron microscopy (SEM) was carried out with a JSM-35CF apparatus (Jeol Ltd) at an accelerating voltage of 25 kV. Samples (powder and tablet) were placed on brass stubs and coated with a sputter-deposited gold film about 20 nm thick using a JFC-1100 ion-sputtering apparatus.

Back-scattering electron (BSE) images were observed to determine the aggregate size distribution of CuO and ZnO dispersed in the matrix of η-Al_2O_3 fine powder. From several enlarged BSE micrographs (see Fig. 5), the aggregate size of CuO or ZnO particles (2000 to 4000 in number) was input as Feret diameter into a computer with a digitizer (Logitec, Mypad-A3-K510mk2 model) and subsequently converted to equivalent volume diameter, which is plotted as volume base-cumulative aggregate size distribution curves in Figs 6 and 7.

Size distribution (Stokes diameter) of η-Al_2O_3, CuO and ZnO particles was measured by gravity sedimentation with a centrifugal automatic particle analyser CAPA-300 (Horiba Co.). Samples were dispersed in water by ultrasonic waves for 5 min before the measurement of equivalent volume diameter. The

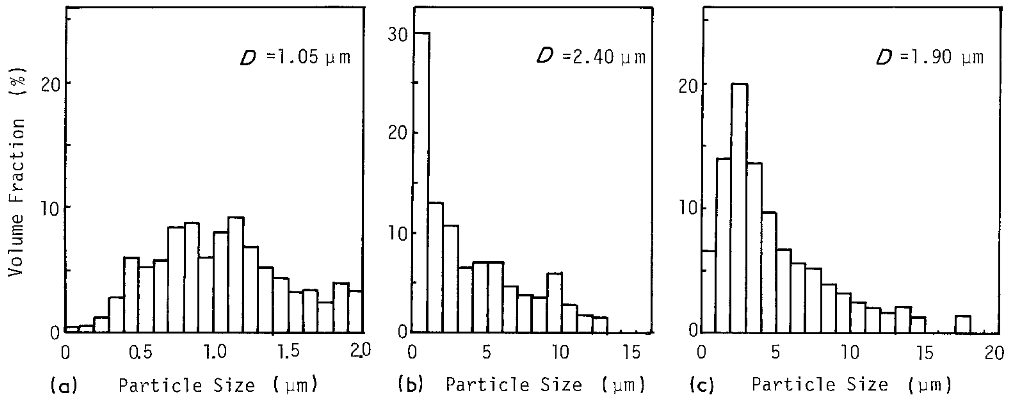

Figure 2 Particle size distribution curves of (a) η-Al_2O_3, (b) CuO and (c) ZnO. Dispersion medium H_2O; D = median diameter.

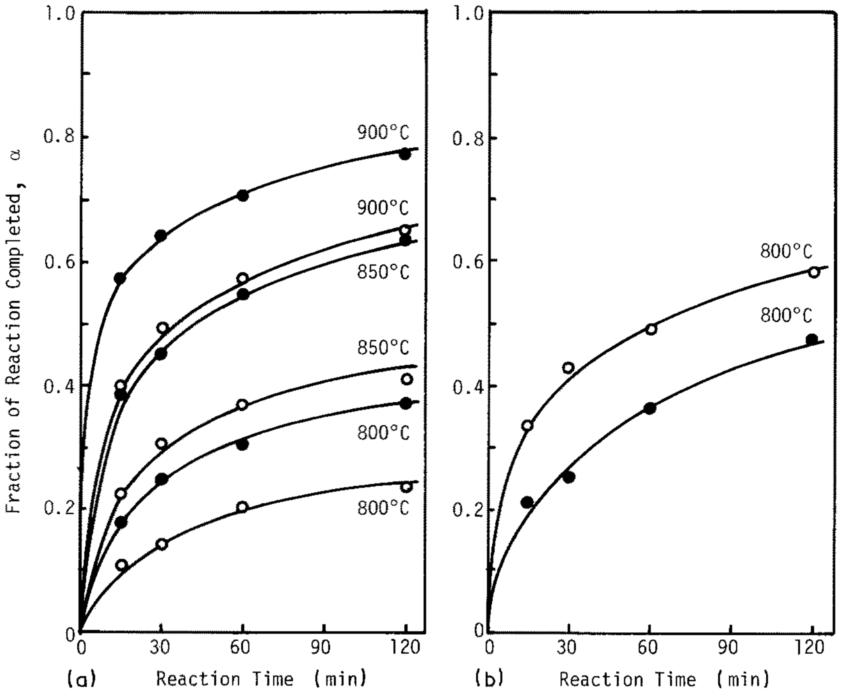

Figure 3 Effect of mixing procedure of reactant oxides on the reaction rate in (a) CuO–η-Al_2O_3 and (b) ZnO–η-Al_2O_3 systems (compaction pressure 0 Pa). (○) Dry mixing in air, (●) wet mixing in ethanol.

measurement was repeated more than three times to obtain a mean diameter.

Specific surface area was determined by the BET method in a Pyrex high-vacuum apparatus.

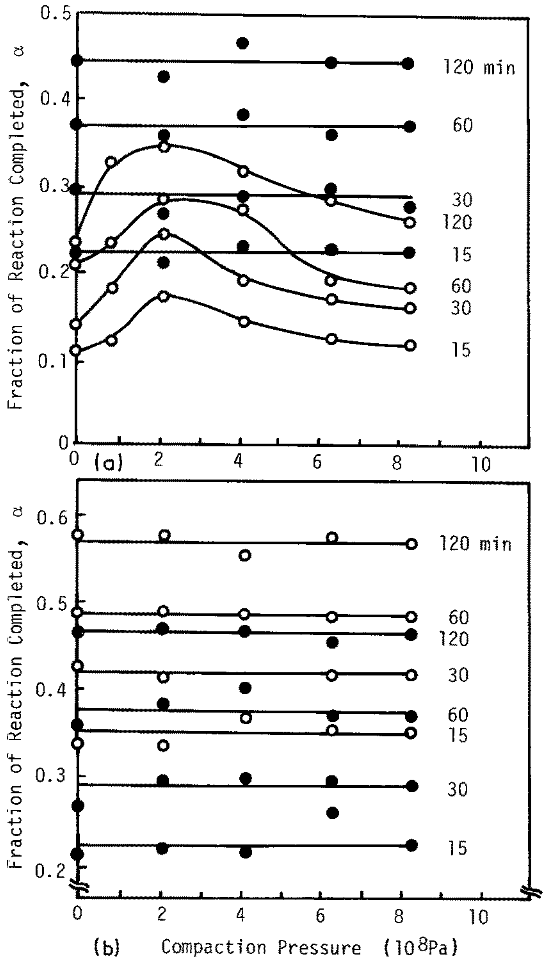

Figure 4 Effect of compaction pressure of reactant oxides on the fraction of reaction completed (α) in (a) CuO–η-Al_2O_3 and (b) ZnO–η-Al_2O_3 systems. Reaction temperature 800° C. (○) Dry mixing in air, (●) wet mixing in ethanol.

3. Results and discussion

Figs 1 and 2 show scanning electron micrographs and size distribution curves of η-Al_2O_3, CuO and ZnO, respectively. η-Al_2O_3 in Fig. 1a shows particles of size less than 1 μm. Its specific surface area is 137 $m^2 g^{-1}$. CuO in Fig. 1b shows a spherical particle of 3 to 5 μm diameter, which is composed of primary particles of 0.3 to 0.6 μm and has a specific surface area of

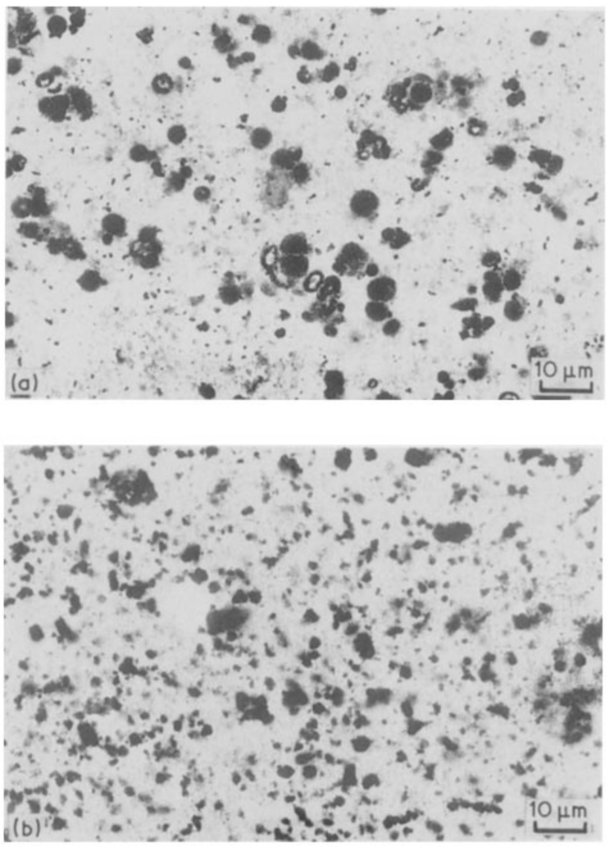

Figure 5 Back-scattered electron (BSE) images for the mixtures of (a) CuO–η-Al_2O_3 and (b) ZnO–η-Al_2O_3 systems. Black area, CuO or ZnO; white area, η-Al_2O_3.

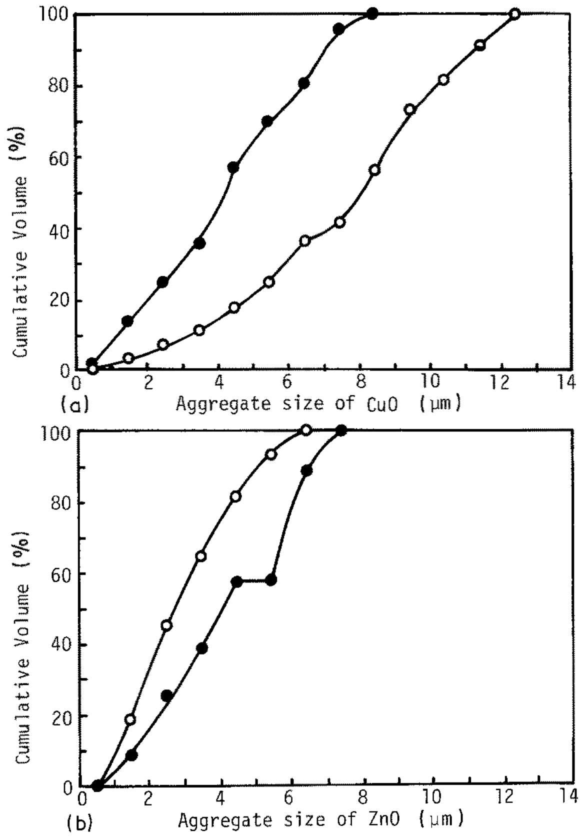

Figure 6 Effect of mixing procedure on the aggregate size distribution of CuO and ZnO in (a) CuO–η-Al$_2$O$_3$ and (b) ZnO–η-Al$_2$O$_3$ systems (compaction pressure 0 Pa). (○) Dry mixing in air, (●) wet mixing in ethanol.

2 m^2 g^{-1}. From SEM photographs of CuO which was impregnated with sulphur [5] and sectioned, though not shown in the figure, it was found that the inside of the spherical particle is often empty. ZnO in Fig. 1c shows a particle of size of 1 to 2 μm which is composed of a primary particle of $\sim$0.1 μm and has a specific surface area of 11 m^2 g^{-1}. The secondary particle size of these samples is in fair agreement with the median diameter (D) shown in Fig. 2.

Fig. 3 shows the effect of mixing procedure (dry or wet mixing) of reactant oxides on the α–t curves for CuAl$_2$O$_4$ and ZnAl$_2$O$_4$ formation. This result was obtained for the uncompacted powder (i.e. at a compaction pressure of 0 Pa). In the CuO–η-Al$_2$O$_3$ system (Fig. 3a), the fraction of reaction completed (α) for the sample obtained by wet mixing is higher than that obtained by dry mixing, whereas in the ZnO–η-Al$_2$O$_3$ system (Fig. 3b) it is reversed. It has already been reported that these data of the reaction rate obeyed the diffusion-controlled Jander's equation [6–8].

Fig. 4 shows the effect of compaction pressures of reactant oxides on the α-values. In the CuO–η-Al$_2$O$_3$ system (Fig. 4a), the α-values obtained for the wet-mixed sample are higher than those for the dry-mixed one and are not influenced by compaction pressures, whereas the α-values for the dry-mixed sample vary with compaction pressures and have a maximum value at 2.1×10^8 Pa. The α-values obtained at reaction temperatures of 850 and 900° C, though not shown in the figure, also showed a maximum value at 2.1×10^8 Pa. On the other hand, in the ZnO–η-Al$_2$O$_3$ system (Fig. 4b), the α-values obtained for wet-mixed samples are lower than those for dry-mixed ones, in contrast to the results in the CuO–η-Al$_2$O$_3$ system, and the α-values for both dry- and wet-samples are not influenced by compaction pressures. The fact that the effects of mixing procedure and compaction pressure on the α-values vary depending on a reaction system, is considered to be explained on the basis of the mixing or dispersion state of reactant oxides.

Table I gives the results which show whether or not the crystallite size of CuO, ZnO and η-Al$_2$O$_3$ in the reactant mixtures is influenced by mixing procedure and compaction pressure. It is found that the crystallite size shows almost constant value regardless of mixing procedure and compaction pressure.

Figs 5a and b show back-scattered electron images of the mixtures of CuO and η-Al$_2$O$_3$ and ZnO and η-Al$_2$O$_3$. The black area corresponds to the aggregate of CuO or ZnO particles and the white one to η-Al$_2$O$_3$. From both photographs the polydispersion of the aggregate of CuO and ZnO can be observed, although these samples were confirmed to be an equimolar mixture by chemical analysis. Thus, from several photographs which were taken of different areas of the tablet, the aggregate size of CuO and ZnO polydispersed in the matrix of η-Al$_2$O$_3$ powder was measured as the Feret diameter and this diameter was subsequently converted to equivalent volume diameter.

Figs 6a and b show the volume base-cumulative aggregate size distribution curves measured for the dry- and wet-mixed samples of CuO–η-Al$_2$O$_3$ and ZnO–η-Al$_2$O$_3$ prepared at a compaction pressure of 0 Pa. The aggregate size of CuO and ZnO converted to equivalent volume diameter is plotted as abscissa and the cumulative volume per cent as ordinate. The left-hand curves in the figure show the fraction of small-sized aggregate is larger. Thus, in the CuO–η-Al$_2$O$_3$ system (Fig. 6a) the wet-mixed sample contains more CuO aggregate of small size than does the dry-mixed sample, but in the ZnO–η-Al$_2$O$_3$ system (Fig. 6b) it is reversed.

TABLE I Effect of mixing procedure and compaction pressure on the crystallite size of η-Al$_2$O$_3$, CuO and ZnO in mixtures of CuO–η-Al$_2$O$_3$ and ZnO–η-Al$_2$O$_3$ systems

	Crystallite size (nm)					
	Mixing procedure		Compaction pressures (10^8 Pa)			
	Dry	Wet	0	0.9	2.1	4.1
CuO $(\bar{2}\,0\,2)$	151.5	156.5	151.5	149.7	152.0	149.2
CuO $(\bar{1}\,1\,3)$	135.0	131.0	135.0	131.3	128.7	128.5
η-Al$_2$O$_3$ (4 0 0)	8.2	8.4	8.2	8.5	8.5	8.4
ZnO (1 0 0)	63.9	65.9	–	–	–	–

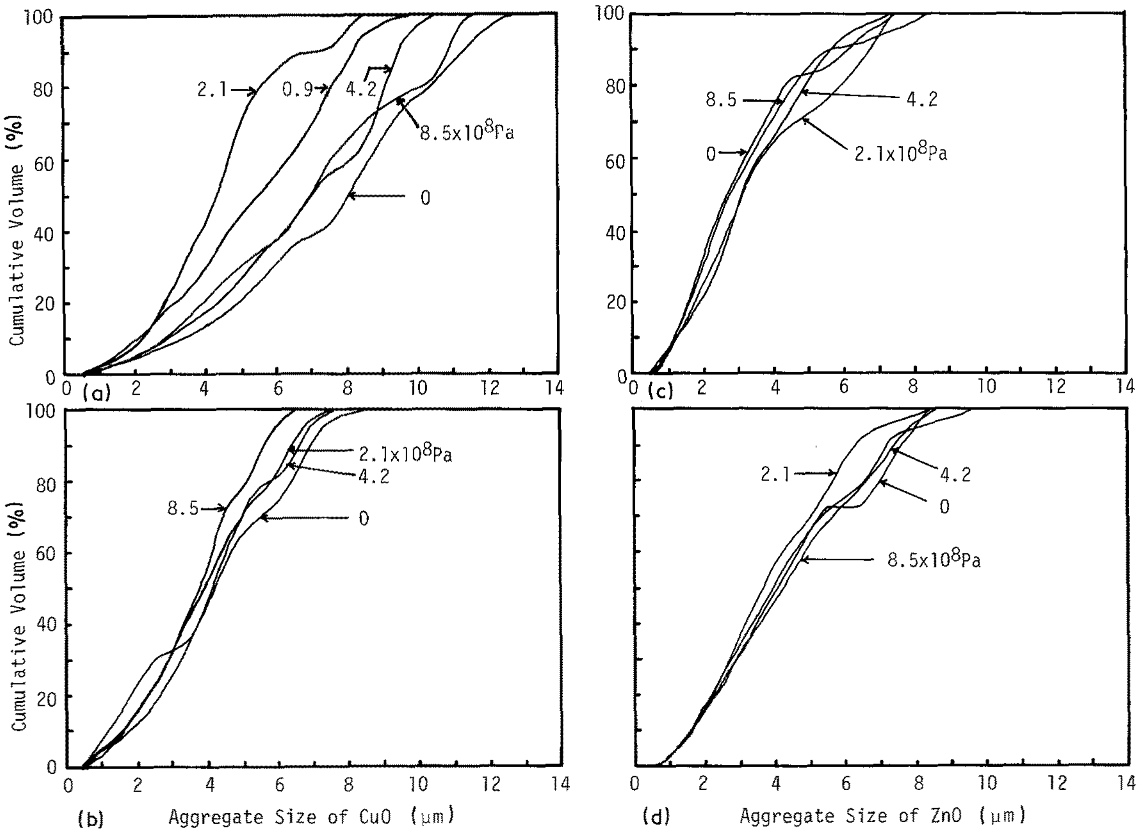

Figure 7 Effect of compaction pressure on the aggregate size distribution of CuO in (a) dry-mixed and (b) wet-mixed systems of CuO–η-Al_2O_3 and of ZnO in (c) dry-mixed and (d) wet-mixed systems of ZnO–η-Al_2O_3.

Fig. 7 shows the cumulative aggregate size distribution curves measured for tablets compacted at various pressures (0 to 8.3 × 10^8 Pa). For the sake of clarity, the experimental points were omitted from the curves. The distribution curves for the wet-mixed sample of CuO–η-Al_2O_3 (Fig. 7b) and for the dry-and wet-mixed samples of ZnO–η-Al_2O_3 (Figs 7c, d) are little affected by compaction pressures. On the other hand, the distribution curve for the dry-mixed sample of CuO–η-Al_2O_3 (Fig. 7a) varies with compaction pressure and shows a maximum distribution of small-sized CuO aggregate at 2.1 × 10^8 Pa. Comparing with the results of α–compaction pressure shown in Fig. 4, the dependence of aggregate size of CuO on compaction pressure shows that the greater the amount of small-sized aggregate is, the higher the α-value.

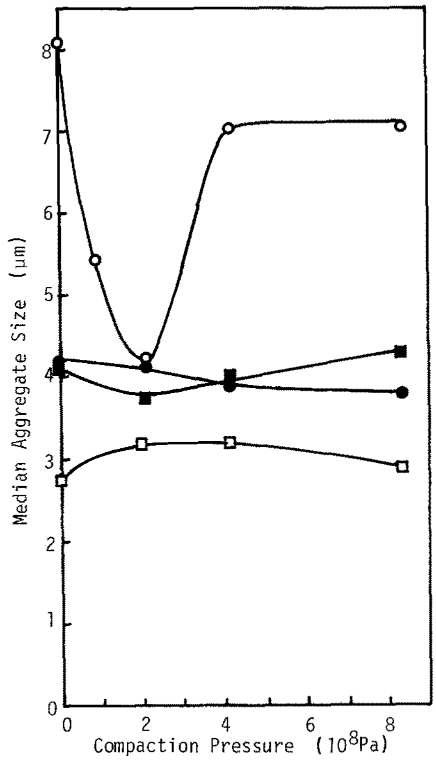

Figure 8 Relationship between compaction pressure and median aggregate size of CuO and ZnO. (○) Dry-mixed system of CuO–η-Al_2O_3. (●) Wet-mixed system of CuO–η-Al_2O_3. (□) Dry-mixed system of ZnO–η-Al_2O_3. (■) Wet-mixed system of ZnO–η-Al_2O_3.

Fig. 8 shows the relationship between compaction pressure and median aggregate size of CuO and ZnO, which corresponds to the size at cumulative volume per cent of 50% in Fig. 7. The median aggregate size of the wet-mixed CuO–η-Al_2O_3 ($\sim$4 μm) is smaller than that of the dry-mixed one (4 to 8 μm), whereas in the ZnO–η-Al_2O_3 system, it is reversed. Comparing these results with those in Figs 3 and 4, it is found that the reaction system in which the fraction of the small-sized aggregate is large leads to high α-values. In addition, the dry-mixed CuO–η-Al_2O_3 shows a minimum median aggregate size (4 μm) at 2.1 × 10^8 Pa, so that it produces a maximum α-value as shown in Fig. 4.

From the above results, the following conclusions can be drawn. The α-values obtained for the samples of CuO–η-Al_2O_3 and ZnO–η-Al_2O_3 vary diversely with mixing procedure and compaction pressure of the reactant oxides. However, it has been found that even if the reaction system is different, the influence of mixing procedure and compaction pressure on the α-value can be explained by the aggregate size of CuO and ZnO dispersed in the matrix of η-Al_2O_3 fine powder. The conditions of mixing in which the particles of the respective reactant powders are not aggregated and are mixed as homogeneously as possible, causes an increase in contact points or contact area between reactant particles, which produces high α-values. Further study is needed to elucidate why the minimum aggregate size of CuO is produced at a compaction pressure of 2.1×10^8 Pa, as shown in Fig. 8.

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