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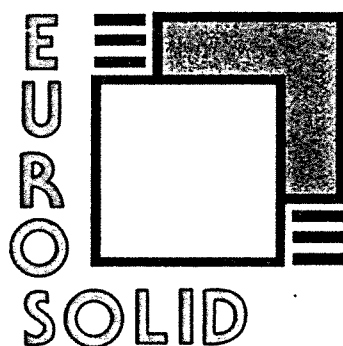
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PREPARED USING A STATIC MIXER AND TRADITIONAL DEVICES**

S. Pagliolico and A.A. Barresi

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# HOMOGENEITY EVALUATION OF MULLITE-ZIRCONIA CERAMICS PREPARED USING A STATIC MIXER AND TRADITIONAL DEVICES

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**Abstract** - The degree of homogeneity of mullite-zirconia composites obtained using different mixing devices is investigated. The performances of a SMXG-Sulzer static mixer are evaluated and compared to those of a stirred vessel and of two milling-mixing devices: the ball mill and the attritor. Two criteria are considered to evaluate the distribution quality, and thus the homogeneity, of the composite: the intensity of segregation, measured by the between-sample variance or indexes derived from it and the scale of segregation, which gives information on the small scale structure.

## Introduction

The spatial distribution of a second phase within the matrix of a ceramic composite system strongly affects the global material properties. For example, the packing density of powders before sintering [1], the sintering kinetics [2] and contraction [3] and consequently the fracture behavior of ceramic-ceramic composites [4] are strongly influenced by the homogeneity of the second phase dispersion. Thus the mixing step is a critical one in the production of composite materials because the properties of the final product will also depend on the small and large scale homogeneity of the powder.

Considering mechanical mixing of different phases, some milling devices can provide effective dispersion and mixing; thus, in the industrial practice, wet comminution and mixing are often carried out simultaneously [5] in order to reduce the size of starting powders and to mix them up. Vibratory and attrition milling produce finer particles and narrower size distributions at a faster rate, but ball milling is usually preferred, even if the energy consumption for fine grinding is higher, for high capacity milling and when mixing with minimum damage to particles is required [6]. The energy consumption of the milling devices is very high, because the kinetic impact energy is only a part of the energy input; therefore their use is justified only if a reduction of the particle size of the original powders must be carried out. In fact, it has to be considered that excessive milling can cause atomic-scale lattice defects and in some cases phase transitions. In addition, very fine powders tend to agglomerate and the formation of aggregates is detrimental for the structural properties of the final material, as they cause the porosity to increase and the coarsening of the grains in the fired body, reducing the mechanical strength of the final product. The previous argumentations justify the research of valid process alternatives to ball mill, not only for laboratory applications but and overall for industrial productions.

In order to compare the mixing performances of different apparatus is important to select appropriate criteria for the evaluation of the composite structure. The randomised state is usually considered as a reference in mixing of powders, as it is the best one that can be obtained; this is actually true only for equally sized and weighted non-interacting particles. If particles of different size and density are mixed, they tend to segregate; on the other side, with cohesive and interacting particles, partially ordered structures can result, especially for

large size differences of the two main components, as the finer particles fill the voids between the coarser particles: of course, the relative size and the relative amount of fine and coarse particles is very important in determining the final structure of the mixture [6-8].

In this work the degree of homogeneity of mullite-zirconia composites obtained using different mixing devices are investigated. Various mixing indexes, modified for the application to sintered ceramics, are considered and evaluated.

The performances of a SMXG-Sulzer static mixer are evaluated and compared to those of a stirred vessel and of two milling devices: the ball mill and the attritor. The application of static mixer succeeded in different industrial processes (alimentary, plastics production, pharmaceutical) but it would be innovative in the ceramic industry, particularly when a grinding action is not required or is detrimental, as it allows continuous operation with very low residence time (high productivity) and reduced energy consumption [9-11]. It can be suggested also when a strict control of the particle size distribution of the different powders that have to be mixed is necessary.

### Experimental procedure

The mullite-zirconia composite (75-25% by volume; 63-37% by weight) has been chosen as a test system, as it is representative of the production of composite materials where a reinforcing phase is dispersed in a matrix, and the distribution of the two phases can be easily analysed on fired bodies by Scanning Electron Microscope (backscattering analysis) thanks to the high difference in the atomic number of zirconium and aluminum. The characteristics of the powders employed are shown in Table 1: the average size of the particles have been measured by a Malvern laser granulometer. Commercial products have been chosen with appropriate size ratio and shape. The mullite, supplied by Baikowski, is constituted by angular and irregular particles. Two different zirconia powders, having different properties have been investigated. The one supplied by Zircar has a shape and a particle size comparable with those of the mullite powder, even if it is slightly smaller, and a theoretical density of 5.6 g/cm<sup>3</sup>. The other one, supplied by Tosoh, has a particle size much smaller than that of mullite ( $d_{50} = 0.3 \mu\text{m}$ ) and a theoretical density of 6.1 g/cm<sup>3</sup>. Tosoh zirconia appears on SEM micrographs as spherically shaped. In order to verify the influence of the variation in the particle size ratio, some batches of mullite and zirconia Zircar powders were separately ground in a ball mill for 48 hours and their mean particle size were respectively 1.3 and 0.3  $\mu\text{m}$  (Table 1). In this way it has been possible to compare the performances of different mixing and grinding/mixing devices, feeding the formers with premilled powders and the latters with raw powders in order to have the same powder granulometry after mixing.

The heteroflocculation technique in water dispersion has been applied: zirconia and mullite have been stabilised in acid (pH = 2.5) and basic (pH = 11.5) solutions respectively. This conditions have been chosen because they correspond to the highest absolute values of slurries zeta-potential, as demonstrated in a previous work [9]. In order to discriminate the effect of heterocoagulation itself, a few runs have been carried out dispersing both the powders in water at pH=11.5. In order to mix equal volumes of slurries, a 19% by weight suspension of zirconia and a 30% suspension of mullite have been prepared; in all cases an ultrasonic probe has been used to favour the powder dispersion (15 minutes at 5 W/cm<sup>3</sup>). The slurries show a dilatant behaviour, but at the tested concentrations the apparent viscosity is low (2-5 mPa s); the heteroflocculation causes a very small increase in the slurry viscosity, that remains below 5 mPa s.

The mixing step has been carried out in four different mixing apparatus: ball mill, attrition mill (or stirred ball mill), agitated system (stirred vessel) and static mixer. The same

Table 1 - Physical properties of the powders.

Materials	Zirconia		Mullite
	Tosoh	Zircar	Baikowski
$d_{10}-d_{50}-d_{90}$ (batches not milled) ( $\mu\text{m}$ )	0.1-0.3-1.5	0.5-1.3-3.5	1.8-3.5-4.8
$d_{10}-d_{50}-d_{90}$ (batches milled) ( $\mu\text{m}$ ) (measured after 48 h milling)	not milled	0.15-0.3-0.5	0.5-1.3-2.5
B.E.T specific surface ( $\text{m}^2/\text{g}$ )	17	5	3.5
theoretical density ( $\text{g}/\text{cm}^3$ )	6.1	5.6	3.2

type of milling balls have been used in the two mills (alumina sphere, diameter 2-2.5 mm), and in both cases the operation has been carried out in batch for 48 hours. The agitated system consisted of a small baffled vessel ( $250 \text{ cm}^3$ ) stirred by a four blade turbine ( $T/D = 2.4$ ) at 300 rpm; operations have been carried out in batch, stirring for 30 min. In the case of the static mixer the operation is continuous: the two slurries are fed concentrically with the same flow rate by a pump to the static mixer, which is realised with 10 Sulzer SMXG mixing elements (10 mm diameter) (see Fig. 1): the total flow rate, in all runs, corresponds to a superficial velocity of  $12.6 \cdot 10^{-3} \text{ m/s}$  (laminar regime), which gives a residence time in the apparatus of less than 8 s. The mixing elements have been realised in stellite, and are connected each one rotated of  $90^\circ$  with respect to the previous one. The elements cause the subdivision, the diversion and recombination of the streams, creating a fine laminated structure that assures a very efficient contact between the phases.

After mixing, the powders have been dried, sieved at  $180 \mu\text{m}$  to remove eventual large aggregates, uniaxially pressed at 200 MPa and sintered at  $1600^\circ\text{C}$  for 3 hours. The

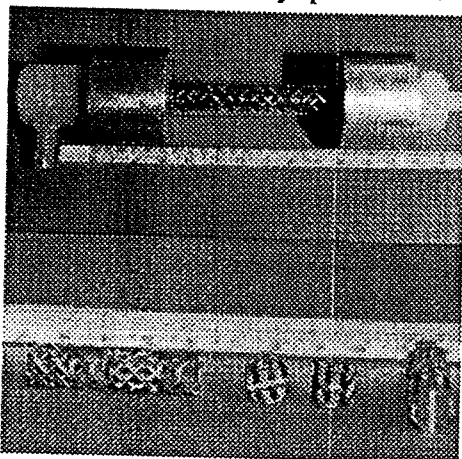


Fig. 1 - The Sulzer SMXG static mixer.

specimens have been polished to  $1 \mu\text{m}$ , thermal etched at  $1550^\circ\text{C}$  for 6 minutes (to evidence the grain boundaries) and observed by a scanning electron microscope in backscattering, to make the grain of mullite and zirconia distinguishable. Grain sizes have been measured by a lineal intercept technique modified for two-phase polycrystalline ceramics [12].

#### Evaluation of the homogeneity of the composite

Two criteria are considered to evaluate the distribution quality, and thus the homogeneity of the composites, according to the suggestion by Danckwerts [13]: the intensity of segregation, which is related to the differences in composition throughout the mixture and is measured by the between-sample variance or indexes derived from it and the scale of segregation, which gives information on the small scale structure and describes the state of sub-division of the clumps. The variations in the intensity and scale of segregation for a two component mixture are illustrated in Figure 2; diffusion effects are responsible for the reduction of the segregation intensity, while the scale of segregation is reduced by convection. It is particularly important to take into account both these parameters when different mixing devices are compared: mixing in the static mixer is purely

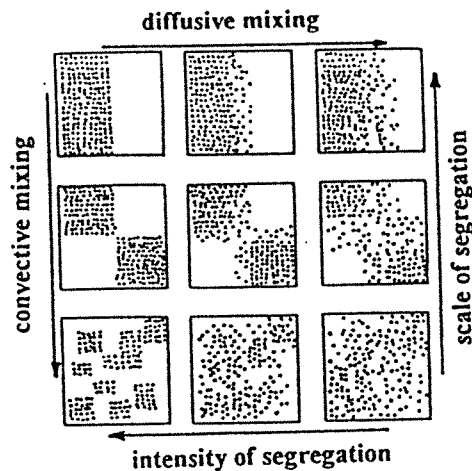


Fig. 2 - Illustration of mixing mechanisms [15].

The short range structure can be quantitatively evaluated using autocorrelation techniques [14, 15]. The usefulness of this approach for the evaluation of the quality of sintered materials has been shown by the authors in a previous work, where the proper choice of the grid size has also been discussed [10]. For a mixture of two components the normalised coefficient of correlation,  $R(r)$ , for all points separated by distance  $r$  is defined by:

$$R(r) = \frac{\overline{(x_i - \bar{x})(x_{i+r} - \bar{x})}}{\sigma^2} \quad -1 \leq R(r) \leq 1$$

where  $x_i$  is the composition at point  $i$ ,  $x_{i+r}$  the composition at point  $i+r$  distant  $r$  from point  $i$ ,  $\bar{x}$  the mean composition and  $\sigma^2$  the variance. The curve  $R(r)$  is called the correlogram; its shape gives many information on the mixture structure, evidencing if and which type of correlation exists between points of the sample at different distances. If the curve falls remaining close to the  $y$ -axis, and then remain zero, the mixture is very close to the random state; the area below the curve, up to the point where it first cross the  $x$ -axis, gives the value of the segregation scale,  $S$  (see Table 3). Eventual oscillations in the curve at long distances are indicative of a partially ordered mixture or of long range segregation.

A few examples of correlograms are shown in Figure 3. The use of the full correlogram for evaluation purposes is not practical, even if it gives more information than the simple scale of segregation. Employing a technique proposed by Horwitz and Shelton, it is possible to compare the obtained correlogram to that of a standard structure; if the random mixture

is chosen for reference, the similarity coefficient has the form:  $S_{sim} = \frac{1}{[\sum R(r)^2]^{1/2}}$  [14, 15].

This coefficient can be used as an index of the mixture structure; it lies between 0 and  $\pm 1$  and is equal to unity if the correlogram is equal to the reference one (i.e. if the mixture is random). From the correlogram it is also possible to evaluate the volume scale of segregation [13]:  $V = 2\pi \int_0^{\zeta} r^2 R(r) dr$  where  $R(\zeta) = 0$ . Danckwerts suggested to use the

ratio  $V/S$  or  $3V/4\pi S^3$  to get information on the shape of the aggregates, in order to distinguish between "streaky" and "no-streaky" clumps. For a linear correlogram, in fact,  $V$  would be equal to  $4\pi S^3/3$ , i.e the volume of a sphere of radius  $S$ , the scale of segregation; thus when the clumps are not extremely elongated or when the mixture is mottled rather than streaky,  $3V/4\pi S^3$  is close to one.

The intensity of segregation is related to the between-sample variance,  $\sigma^2$ . A large

convective, while in a stirred vessel both convection and diffusion are relevant; in the mills, "shear mixing", that is a combination of the previous two mechanisms, occurs.

In order to evaluate quantitatively the quality of the distribution, a  $32 \times 32$  square grid has been superimposed to the SEM micrographs ( $\times 4000$ ). The grid size corresponds to  $0.5 \mu\text{m}$ , which is significantly smaller than the average grain size; it can be remembered that, in order for a clump to be resolved, it has to be at least three times as large as the sample interval.

In this work the scale and the intensity of segregation have been measured independently.

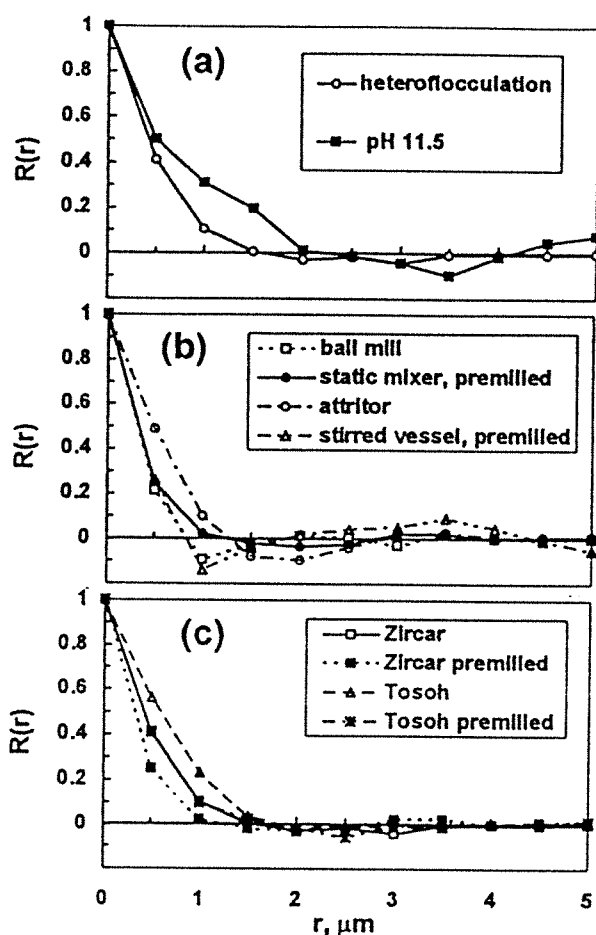


Fig. 3 - Correlograms of different composites. a) Zirconia Zircar in static mixer: effect of heteroflocculation. b) Zirconia Zircar: comparison of different devices. c) Static mixer: effect of particle size (raw powder; mullite and Zircar both premilled; raw Tosoh and mullite premilled).

application to sintered ceramic materials, unit samples formed by a single grid cell ( $0.25 \mu\text{m}^2$ ) have been considered; larger samples have been obtained taking square samples

number of indexes based on this parameter (or on the standard deviation,  $\sigma$ ) have been proposed; reviews, with the discussion of the characteristics of the various indexes can be found in the literature [16-19].

The indexes proposed in the literature generally take the variance values of the segregated and random mixture as a reference, but they all depend, even if to a different extent, on the sample size and mixture ratio. In evaluating the usefulness of the different indexes for assessing the quality of the mixture the dependence on the mixture composition must be taken into account, together with the index sensibility. A few indexes, which from a literature survey seemed to give the best performances, have been selected and listed in Table 2;  $\sigma$  is the standard deviation of the actual mixture,  $\sigma_r$  that of the random mixture and  $\sigma_0$  is the standard deviation corresponding to the unmixed material [17, 20]. Figure 4 shows a comparison of the various indexes for some composites and their dependence on the sample size. The variance based indexes have been originally defined for dry powders, and refer to samples composed by a fixed number of particles,  $N$ . For the

Table 2 - Mixing indexes.

Index		ref.	limiting values		
			unmixed	random	ordered
Rose	$1 - \sigma / \sigma_0$	[21]	0	$1 - \sigma_r / \sigma_0$	1
Rose; Yano & Sano	$1 - \sigma^2 / \sigma_0^2$	[21]	0	$1 - \sigma_r^2 / \sigma_0^2$	1
Asthon & Valentin	$\sqrt{\frac{\log \sigma_0^2 - \log \sigma^2}{\log \sigma_0^2 - \log \sigma_r^2}}$	[22]	0	1	$\infty$
Valentin	$\frac{\log \sigma_0 - \log \sigma^2}{\log \sigma_0 - \log \sigma_r}$	[23]	0	1	$\infty$
Carley-Macaulay & Donald	$\frac{\sigma^2 - \sigma_r^2}{1 - \frac{1}{N}}$	[24]	$> 0$	0	$< 0$

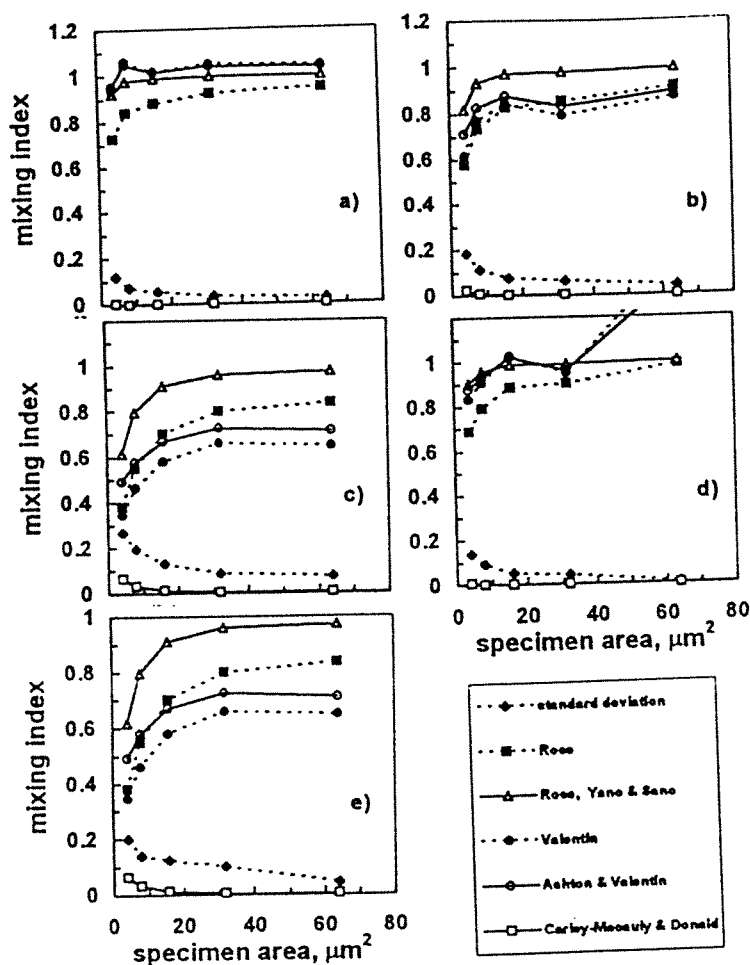


Fig. 4 - Comparison of different mixing indexes: a) Zircar, heteroflocculation in ball mill; b) Zircar, heteroflocculation in static mixer; c) Tosoh, heteroflocculation in static mixer; d) Zircar, powders premilled, heteroflocculation in static mixer; e) Zircar, dispersion at pH=11.5 in static mixer. Full lines refer to variance based indexes; dashed lines to indexes using standard deviation.

the index evaluated at a fixed sample size to compare the different mixtures. In Table 3 the values of the Rose index evaluated for two different sample sizes have been reported.

### Results and discussion

The comparison of the performances of the different mixing devices is carried out considering separately zirconia-Zircar and zirconia-Tosoh composites (Table 3) because of the large differences between the two types of powders.

1) The homogeneity of the composites depends on the relative dimension of the particles of the two phases and this can be seen comparing the bodies prepared in the static mixer with powders of different size ratio. When the particle mean size ratio of the zirconia Zircar/mullite varies from  $0.3/1.3 = 0.2$  to  $1.3/3.5 = 0.4$  and to  $1.3/1.3 = 1$  (respectively composites 3, 1, 4) the segregation scale ranges from 0.39 - very low value- to 0.51 and 0.45 and the Rose index (at  $4 \mu\text{m}^2$ ) ranges from 0.69 to 0.57 and 0.59. A size ratio equal to 0.2 seems to favour more randomised structures. When the zirconia Tosoh/mullite size ratio

composed of  $N$  units. It must be observed that for a random mixture the variance is inversely proportional to  $N$ , while for a segregated material it is independent of the sample size; for a non-random mixture the dependence of the variance (and therefore of the indexes derived from it) is influenced by the type of correlation inherent in the mixture and on the type and shape of the sample [25].

Comparing the performances of the different indexes it appears that the one proposed by Carley-Macaulay and Donald is one of the most rigorous, but has a very low sensibility. Those proposed by Valentin seem very sensitive to small errors in the evaluation, and are not bounded: in fact, for partially ordered mixtures the indexes tend to infinite. Thus the indexes proposed by Rose seems preferable; in particular the one based on the standard deviation has been selected, because in general the indexes based on this parameter are more sensible than those based on the variance. It is convenient to use the value of

varies from  $0.3/3.5 = 0.1$  (composite 8) to  $0.3/1.3 = 0.2$  (composite 9) the segregation scale ranges from 0.66 to 0.52 and the Rose index ranges from 0.38 to 0.57. Also in this case a higher homogeneity is reached when size ratio is equal to 0.2. On the other hand it has to be pointed out that the differences between the previous parameters are not so important and that the static mixer performs well also when starting powder size ratio ranges from 0.2 to 1. As shown in the last column of Table 3, in order to carry out a comparison between different specimens using a variance based index it is very important to use always the same sample size. It can be seen that the sensitivity of the Rose index is approximately the same in the range  $4 - 32 \mu\text{m}^2$ ; the apparent discrepancies that can be observed if the composites are ordered by their Rose index are due to the different variance-sample size relationships in the different specimens. Of course the reference values for discriminating between good and poor mixing must be determined empirically for each sample size and for each application, according to the procedure suggested by Boss [17].

2) As the powder granulometry influences the body characteristics, and the size of the powders is reduced in the ball mill and the attritor by their grinding action, the previous devices are better compared to stirred vessel and static mixer when the latter are fed with premilled zirconia and mullite powders (comparison between composites 3, 5, 6, 7 and between composites 9, 10, 11, 12). In the case of zirconia-Zircar ball mill and static mixer allow to obtain composites with the highest homogeneity (scale of segregation,  $S_{AB}$  and Rose index close to random values). From Table 3 it results that ball mill is the better performing apparatus also when zirconia-Tosoh is used; note that in this case there is no further reduction of the mean particle size of the zirconia, because it is below the grinding critical size.

3) All the composites now considered show similar characteristics with homogeneity parameters very close to those of a random distribution (in a few cases, with Zircar in ball mill and static mixer even slightly better): the apparatus used in this work are high efficiency mixing devices when the heteroflocculation technique is employed. It must be noted that the scale of the aggregates is generally of the same scale of the grain size, or intermediate

Table 3 - Characteristics of the composite materials.

Device	Mix Nr.	Powder $d_{50}$ , $\mu\text{m}$		Composite grain size $\mu\text{m}$		S $\mu\text{m}$	$S_{AB}$	V $\mu\text{m}^3$	$\frac{3V}{4\pi S^3}$	Rose index	
		Zir	Mul	Zir	Mul					$4 \mu\text{m}^2$	$32 \mu\text{m}^2$
<b>ZIRCAR</b>											
static mixer	1	1.3	3.5	1	1.4	0.51	0.92	0.68	1.2	0.57	0.86
	2*	1.3	3.5	1	1.2	0.76	0.84	2.88	1.6	0.54	0.76
	3	0.3	1.3	0.8	0.7	0.39	0.99	0.24	1.0	0.69	0.90
	4	1.3	1.3	1	1	0.45	0.88	0.54	0.9	0.59	0.82
stirred v.	5	0.3	1.3	0.8	1	0.38	0.88	0.13	0.7	0.68	0.85
ball mill	6	1.3	3.5	0.9	1	0.34	0.97	0.12	0.7	0.73	0.92
attritor	7	1.3	3.5	1.3	1.4	0.53	0.89	0.61	1.0	0.58	0.93
<b>TOSOHO</b>											
static mixer	8	0.3	3.5	2	1.5	0.66	0.83	1.37	1.1	0.38	0.8~
	9	0.3	1.3	1.4	1.3	0.52	0.92	0.76	1.3	0.57	0.84
stirred v.	10	0.3	1.3	1.2	1.2	0.54	0.91	0.92	1.3	0.55	0.74
ball mill	11	0.3	3.5	1.5	1	0.46	0.93	0.41	1.0	0.61	0.85
attritor	12	0.3	3.5	1.3	1.3	0.49	0.91	0.46	0.9	0.59	0.83
Legenda: * dispersion in water at pH = 11.5; $d_{50}$ , average particle size; S, linear segregation scale; $S_{AB}$ , similarity coefficient; V, volumetric segregation scale;											

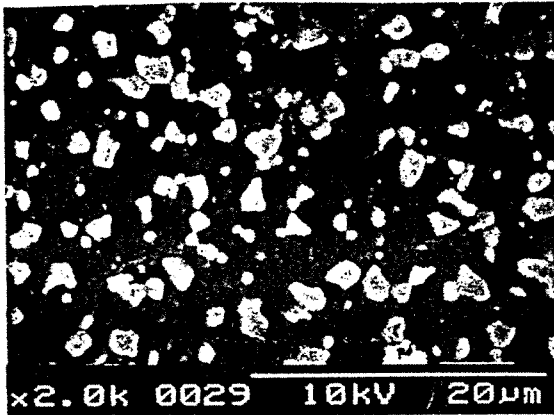


Fig. 5 - Micrograph of composite mullite-zirconia Zircar, heteroflocculation in static mixer

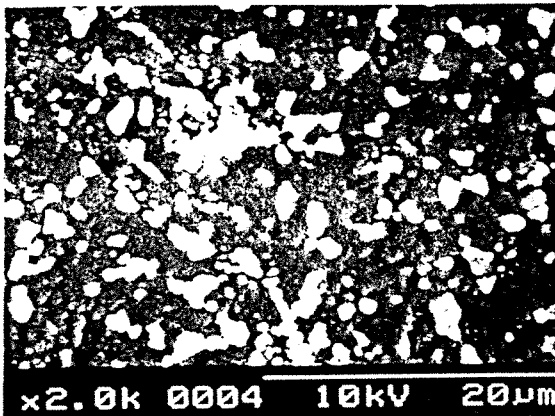


Fig. 6 - Micrograph of composite mullite-zirconia Zircar, dispersion at pH = 11.5 in static mixer.

between the grain size of the two phases in case they are very different: this indicates that the two powders are well distributed. Of course it has to be taken into account that the scale of segregation is related to the radius of the clumps, and that the measure of the grain size has an uncertainty of  $\pm 0.2 \mu\text{m}$ .

4) On the contrary, the segregation scale of composites 1 and 2 obtained in the static mixer by heteroflocculation (Fig. 5) and by stabilisation of both mullite and zirconia slurries at pH=11.5 (Fig. 6) are considerably different (respectively 0.51 and 0.76). This difference is evidenced by the comparison of the correlograms shown in Fig. 3a. The stabilisation of slurries is thus very important and heteroflocculation can significantly improve the intimate mixing.

5) Finally all the composites considered show the  $3V/4\pi S^3$  ratio close to 1, a value typical of non streaky structures.

### Conclusion

The results evidence that the employment of a static mixer appears very promising,

as it allows continuous operations and it assures very good macromixing, with very low residence times and energy consumption. Also the microscale mixing is better than in a stirred vessel and generally comparable (or even better in some cases) to that obtainable with devices in which a grinding action takes place. The size ratio of the starting powders does not affect markedly the homogeneity obtained in the static mixer while the heteroflocculation technique can significantly improve intimate mixing. Non streaky structures have been obtained in all the cases considered.

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