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Reliability study of ceramic matrix composites based on clinker portland doped with alumina and silica

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A study was made of the Weibull modulus of white clinker portland reinforced with alumina and silica. The Weibull distribution was introduced as a way of measuring the reliability of materials through the slope or shape parameter, known as Weibull modulus, and it is used as a reference and estimation of the probability of failure. The manufacturing process of composite materials (3, 6 and 9% Al_2O_3 and SiO_2 by weight) includes mixing in a ball mill, cold isostatic pressing in wet bag at 180 MPa and sintering at 1400°C in air. Bending strength was used as the key property for measuring the Weibull modulus using more than 20 tests in all cases. The correlation coefficients obtained in all the estimations for the studied materials are above 95%. These ceramic matrix composite (CMCs) materials present a high Weibull modulus (in some materials about 26) and better behaviour than plain white clinker portland. Most results are above typical values of the conventional and advanced ceramics (between 5 and 15). Microstructural analysis was carried out to explain the reliable behaviour of these materials, a behaviour that could make them very interesting for structural applications. © *2000 Kluwer Academic Publishers*

1. Introduction

Reliability is no more than the extension of the operational quality aver a period of time, that is to say, the conservation of properties, its definition is associated with the failure probability or survival. In materials strength, reliability would be associated with the most probable value of the mechanical property evaluated, and it would be higher as the amount of abnormal values decreases or the resulting interval of values becomes the shortest possible. As a function of the mechanical basic properties and the reliability of the material, the best application could be found.

The results obtained for a given test on a perfectly characterised material (composition, processing and quality level) present a certain dispersion in their values. This dispersion is not totally attributable to the test procedure, but indicates a statistical behaviour of the material, due to chance intrinsic variables not entirely dependent on material characterisation. In ceramic materials and CMCs, the mechanical values obtained usually present a greater dispersion than that found in metallic materials.

New technologies have made ceramic and CMCs less brittle and more reliable; they maintain their properties and are not bound by motives of their reliability or elevated costs of production. Valued for their refractory, magnetic, optic [1], electric [2, 3] or electronic [4] properties, their use is restricted by their reliability and it is necessary to know their strength values and their distribution of defects [5].

The most common defects in ceramics are found on surface (such as roughness) and in volume (pores, inclusions). For example, defects smaller than 50 μm are not easily detectable by non-destructive tests and could lead to component failure [5]. Volume defects produces more homogeneous values than the superficial defects. The latter give rise to breaks and sometimes to values below than the minimum strength permitted. The relationship between the final roughness of the part and its strength is very high. The strength diminishes with the increase of roughness and relies on the polishing direction. In addition, the average strength depends on the size of the sample, since it is probable that large size defects exist in a greater volume. This effect is applicable to both on composite and monolithic materials.

A number of studies have been made of the reliability of different composite materials: SiC [6] (with Weibull modulus between 8 and 10), alumina [7], Al_2O_3/ZrO_2 [8], alumina fibres [9], giving special attention to the variations of fibre diameter to determine to Weibull behaviour. Brittle fibres, with low fracture toughness, present Weibull modulus between 2 and 5 with a high dispersion of results. Typical modulus values for glass fibres oscillate between 5 and 15, with a lower dispersion. For monolithic and polycrystalline ceramics, the interval reaches 25 [10]. Studies of CMC

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reliability based on clinker reinforced with Al_2O_3 and SiC [11, 12], show that the reliability of these ceramics follows a Weibull distribution and their modulus oscillates between 8 and 15.

Properties related to the strength of the materials need a great number of tests to establish the distribution function and find a reliable survival parameter. The results establish a curve of distribution corresponding to reliability. The Weibull distribution is the most commonly used, although for fibres more parameters are required than the two, as in Weibull statistics. The Weibull distribution is used when the failure risk of the component is acceptable. The use of statistical models requires samples reflect the distribution of defects of the material.

The Weibull is the function of probability that best approaches the behaviour of mechanical and electromechanical components. A brittle material could have more than one defect; in fact, defects exist of different sizes, forms and orientations in relation to the applied load. The Weibull distribution is often used to determine the dispersion of mechanical results in brittle materials [13].

Randomly distributed defects, in CMCs with brittle behaviour, conform to statistical considerations. The failure probability depends on Weibull distribution, and the resistant properties of a polycrystalline composite material could be expressed through the parameters of the Equation 1:

$$F = 1 - \exp\left(-\alpha\, \sigma^{\beta}\right) \tag{1}$$

where σ is the applied tension, F is the probability of failure, β is the Weibull modulus (a dispersion measurement) and α is scale parameter. If the same size (V_E) is considered for all the samples, then α and β could be determined graphically by logarithms and finally, the Equation is 2:

$$\mathrm{Ln}\,\mathrm{Ln}\frac{1}{1-F} = \beta\,\mathrm{Ln}\,\sigma_{\max} - \mathrm{Ln}\,\frac{\sigma_0^{\beta}}{V_E} \tag{2}$$

a lineal equation where failure probability is related to the applied load, where β is the slope representing the dispersion for each material and α is scale factor that is represented by $\mathrm{Ln}\,\sigma_0^m / V_E$.

2. Experimental procedure

Composite materials were manufactured by the conventional methods of consolidation of conventional and advanced ceramics. Tables I and II show the characteristics of the white clinker employed as base material (supplied by Valenciana de Cementos - Spain -) and the characteristics of the added reinforcements.

TABLE I Characteristics of white clinker employed

Composition by oxides		Mineralogical composition	
%SiO_2	22.90		
%Al_2O_3	6.60		
%Fe_2O_3	0.30	%C_3S	53.87
%MgO	0.94	%C_2S	25.10
%Sulphates	0.92	%C_3A	16.98
%CaO	67.70	%C_4AF	0.912
%CaO free	0.70		
%K_2O	0.10		
%fire losses	0.58		

TABLE II Characteristics of added reinforcements

Additives	Powder characteristics
α - Al_2O_3	Purity: 99.9%, 98% $< 2\,\mu$m. Density: 3.9 g/cm^3. Alcoa (Brasil)
SiO_2	Amorphous. Purity: 99%. Density: 2.65 g/cm^3. Crosfield Chemicals. (UK)

White clinker was mixed with the different additives (Al_2O_3, and SiO_2), in proportions of 3, 6 and 9% by weight by dry mixing in a ball mill during 30 minutes, using stainless steel balls with a diameter of 10 mm. The ratio in weight between material and balls was 1/5. The homogeneity of the different mixtures was then checked.

The ceramic mixtures, as well as the plain clinker portland, were encapsulated in flexible plastic moulds and the air was eliminated in avoid the formation of pores. Subsequently, the samples were produced by cold isostatic pressing (CIP) in wet bag, under pressure of 180 MPa. The materials were sintered in air at a temperature of 1400°C, optimised in a previous work [14]. Finally, the samples were cut to adequate dimensions ($3 \times 3 \times 25$ mm $\times$ mm $\times$ mm) for bending strength tests. A complete microstructural study was carried out to determine the influence of reactions between the reinforcements and the white clinker.

The three points bending strength was determined by MPIF Standard 41-91 [15]. Brittle materials are very sensitive to surface defects. To avoid errors due to surface roughness, the load was applied on the surface with lower roughness, which was uniform in all the materials. The Weibull modulus was evaluated using bending strength as the key value.

A number of methods give a reliable approach to the Weibull modulus, most of which use one of the estimators of the failure probability [16]. In this work, F_j was chosen as the estimator of the probability of failure:

$$F_j = \frac{j}{(n+1)} \tag{3}$$

where j = rank of the experiment and n = total number of experiments.

Once estimated the probability of failure, and being σ_j the bending strength value of the j experiment, we fit a lineal regression as (4):

$$\mathrm{Ln}\,\mathrm{Ln}\left(\frac{1}{(1-F_j)}\right) = A + m\,\mathrm{Ln}\ \sigma_j \tag{4}$$

The slope "m" of Equation 4 is the Weibull modulus. For good lineal adjustment, a number of experiments are required. In this work, for each material at least 20 experiments were made.

3. Results and discussion

The most significant result of these CMCs is their high Weibull modulus, as seen Fig. 1. Table III summarises the values of bending strength. A maximum Weibull modulus value close to 27 for the 9% alumina added is found, very high compared with the usual values for conventional and even advanced ceramics (between 5 and 15).

The adjusted linear regressions are shown in Figs 2 and 3. These lines show the adjustments carried out for obtaining the Weibull modulus of the studied materials at optimal sintering temperature, on 20 samples of each material. A higher slope represents a greater Weibull modulus, while a higher abscissa represents a greater bending strength of the material. The correlation coefficients of all materials were above 95%. The statistical parameters of the calculated regressions for the Weibull modulus are detailed in Table IV.

TABLE III Bending strength results for composite materials

Material	Bending Strength (MPa)
White Clinker	65,5
3%	65,5
6% Al_2O_3	86,2
9%	80,1
3%	71,9
6% SiO_2	81,0
9%	70,1

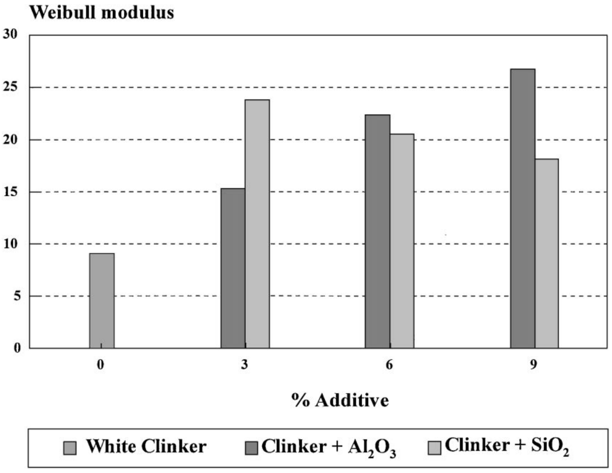

Figure 1 Weibull modulus of the composite materials based on white clinker.

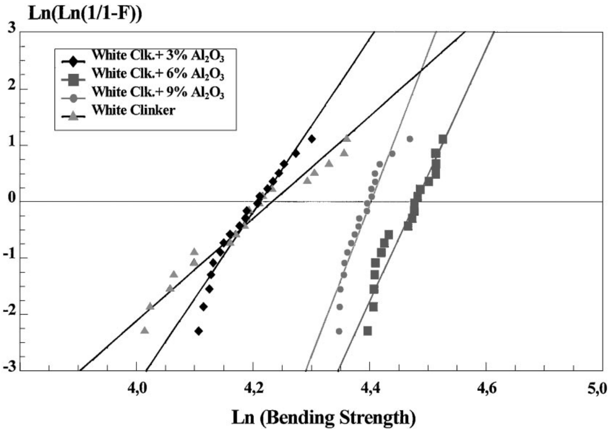

Figure 2 Weibull regressions of materials based on white clinker with Al_2O_3.

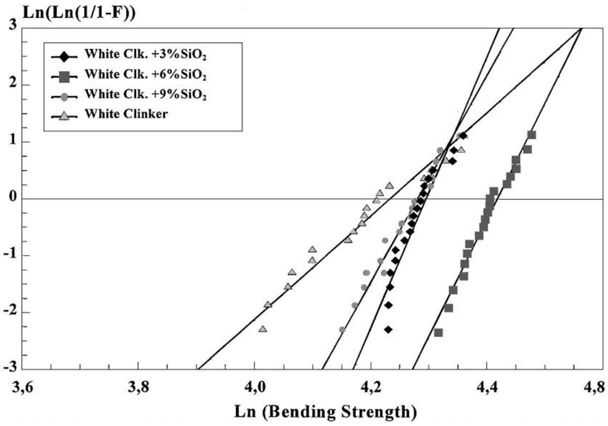

Figure 3 Weibull regressions of materials based on white clinker with SiO_2.

The addition of alumina to the white clinker increases the bending strength (Table III), its values increasing with the amount of added oxide, and also increases the Weibull modulus and the reliability. Maximum strength is obtained with 6% of alumina (Table III), with an elevated Weibull value (Fig. 1). The maximum value of reliability is achieved with 9% of Al_2O_3 (Fig. 1) with a good value of bending strength. This is produced by the reaction between alumina and white clinker, which forms a greater amount of tricalcic aluminate phase, capturing CaO of the clinker and producing a greater amount of belitic (C_2S, $2CaO{\cdot}SiO_2$) phase of small and uniform size (Fig. 4). The presence of C_3A ($3CaO{\cdot}Al_2O_3$) and C_2S has a more positive influence on reliability. These two phases are less brittle than C_3S - $3CaO{\cdot}SiO_2$ - (Table V) [17], so their reliability is higher. The addition of alumina changes the pore morphology (Fig. 5). Clinker has many small pores, and the presence of alumina reduces the number of pores, but they are of larger size. This change in porosity has also a good influence on reliability. The larger addition of alumina also changes porosity from spherical to a more irregular morphology, so the negative effect on Weibull modulus is reduced.

TABLE IV Summary of statistical results of Weibull regressions

Material	Weibull regression	Linear correlation coefficient
White Clinker	$y = -38{,}481 + 9{,}0894x$	0,9796
3%	$y = -64{,}598 + 15{,}334x$	0,9782
6%Al_2O_3	$y = -100{,}14 + 22{,}355x$	0,9552
9%	$y = -117{,}87 + 26{,}776x$	0,9587
3%	$y = -102{,}05 + 23{,}757x$	0,9597
6% SiO_2	$y = -90{,}879 + 20{,}569x$	0,9910
9%	$y = -77{,}847 + 18{,}183x$	0,9833

TABLE V Hardness and brittleness ratio for main phases of clinker [17]

Phase	H_v(GPa)	K_c($MPa{\cdot}m^{1/2}$)	$H_v/K_c{\cdot}$ ($m^{-1/2}$)
C_3S	7.5	1.7	4700
C_3A	9.0	3.1	2900
C_2S	6.7	3.7	1800
Al_2O_3	12.0	4.0	3000

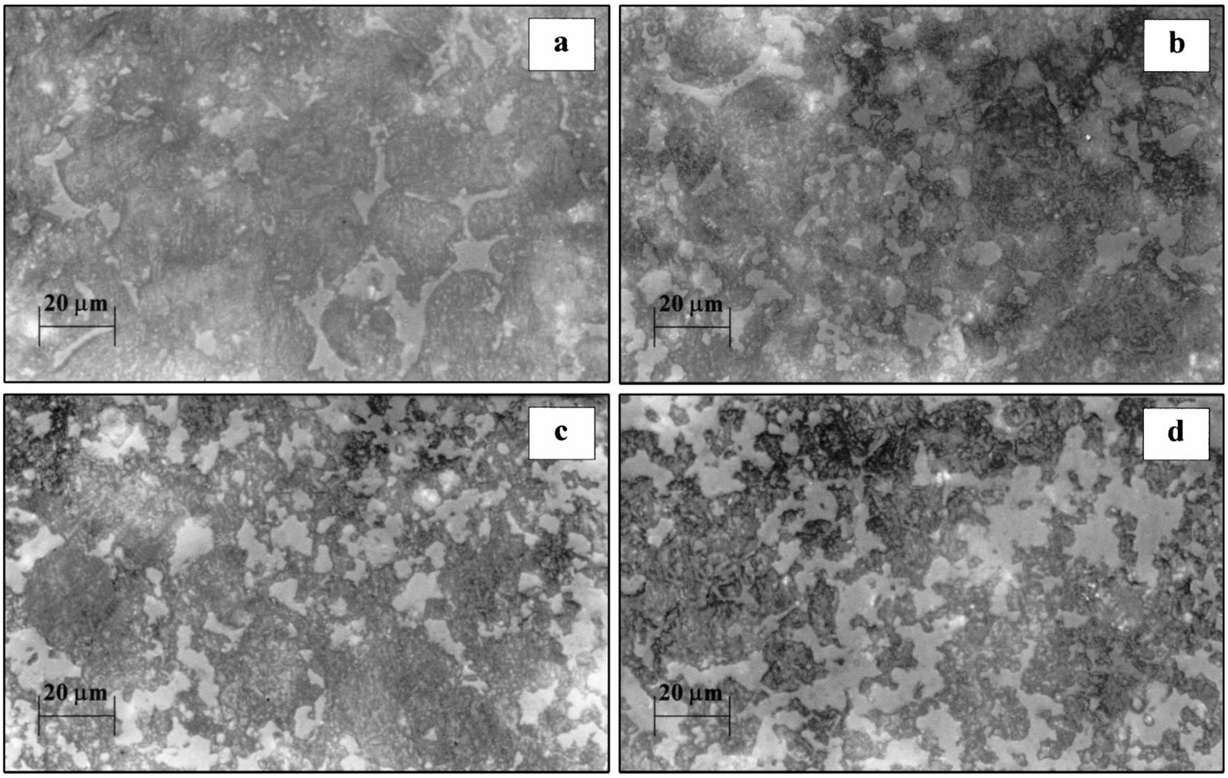

Figure 4 Microstructures of composite materials based on clinker Portland with alumina: (a) plain clinker, (b) 3% of alumina, (c) 6% of alumina and (d) 9% of alumina. Etched with 13% vol. Acetic acid/Ethanol.

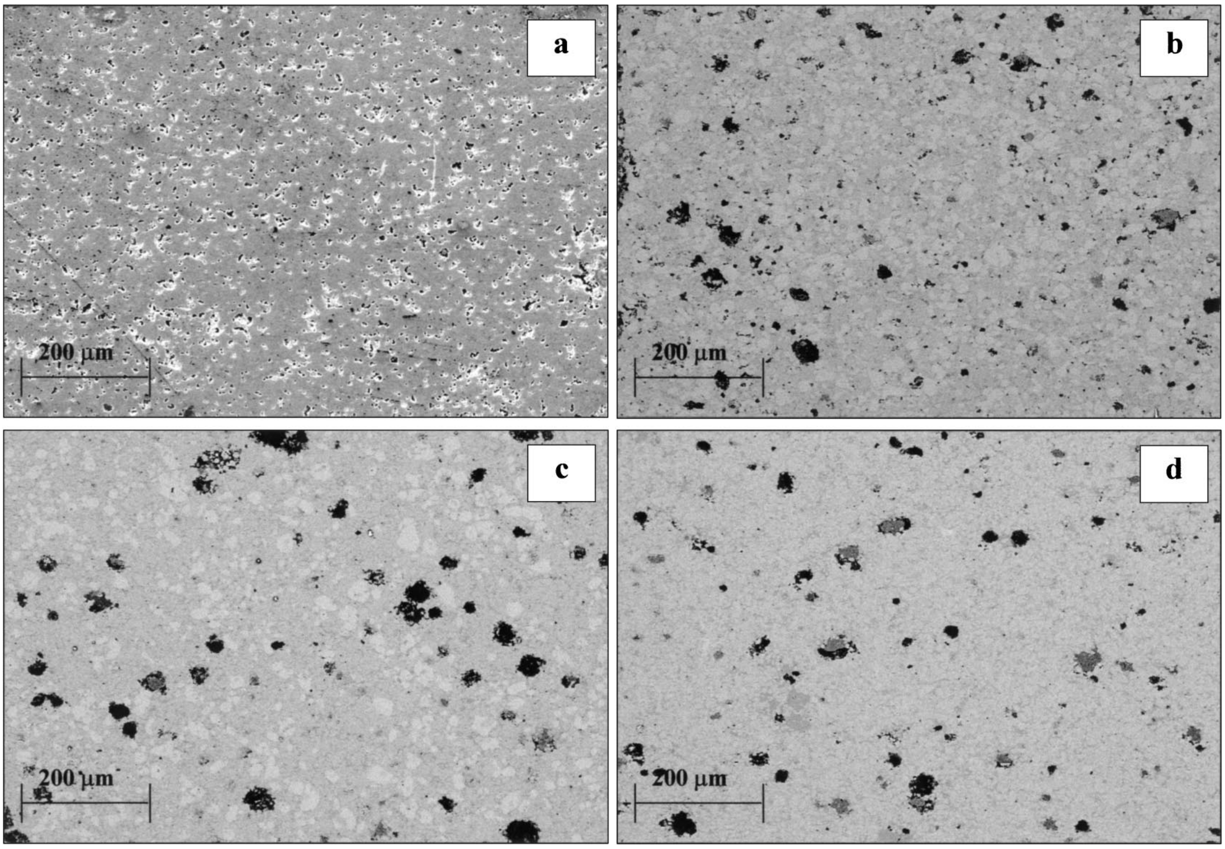

Figure 5 Porosity evolution of composite materials with alumina: (a) plain clinker, (b) 3% of alumina, (c) 6% of alumina and (d) 9% of alumina. Without etching.

The addition of silica produces an increase in the bending strength over that of white clinker (Table III), due to reactions between the clinker and the reinforcement, with a maximum at 6% of SiO_2. The added silica reacts with the white clinker producing an increase of belitic phase (C_2S) and a reduction of the amount and size of porosity (Fig. 6). However, some segregation appears in belitic areas (Fig. 7), which affects both the strength and the Weibull modulus. The Weibull modulus shows a considerable increase for the three materials

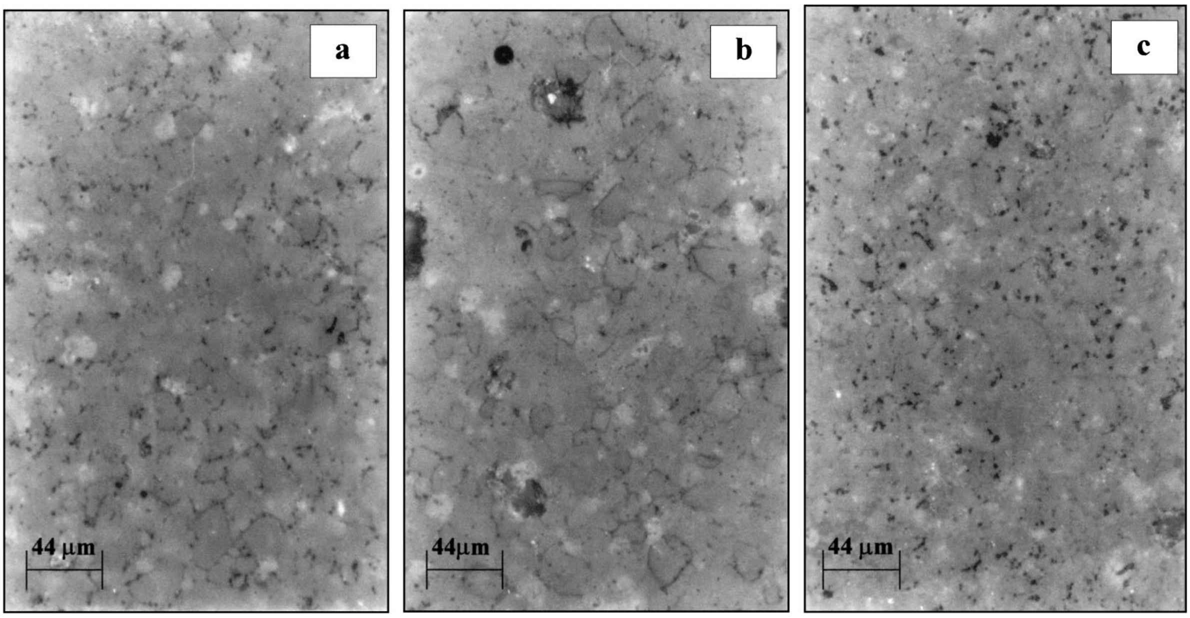

Figure 6 Porosity evolution of composite materials with silica: (a) 3% of silica, (b) 6% of silica and (c) 9% of silica. Etched with 13% vol. Acetic Acid/Ethanol.

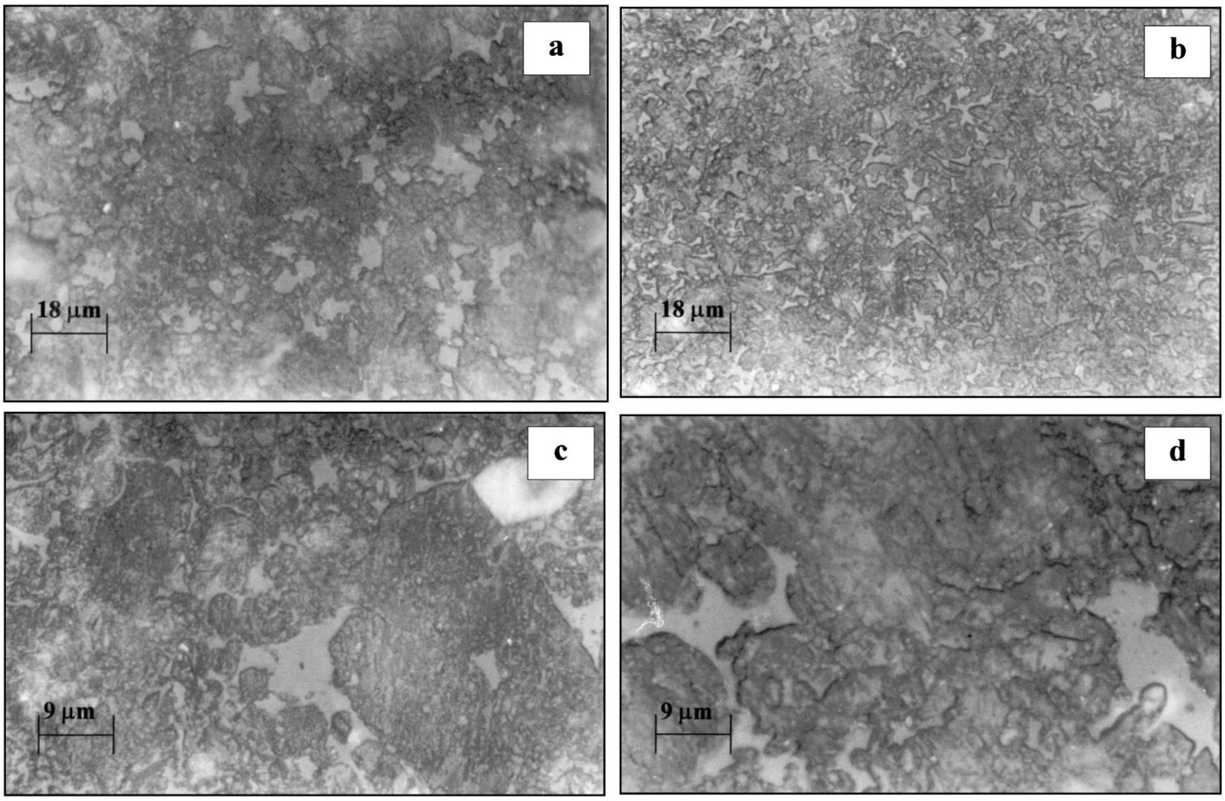

Figure 7 Microstructural evolution of composite materials with silica from (a) 3% of SiO_2, (b) 9% of SiO_2, (c) and (d) details for 6% of SiO_2. Etched with 13% vol. Acetic Acid/Ethanol.

as compared with plain clinker, due to the increase in the amount of less brittle phase (C_2S). However, it diminishes with the increase of silica (Fig. 1), with a maximum for 3% of silica due to these segregations. A material with a good strength/Weibull modulus ratio would be with 6% of SiO_2. The values in all CMCs are very good compared with the reliability of a conventional ceramic [6], while plain clinker behaves like a conventional ceramic (Weibull modulus 9,1).

From the point of view of reliability, composite materials have Weibull modulus values above 15, as shown in earlier studies [11, 12, 18–20]. White clinker reinforced with 6% of alumina (86,23/22,35) and with 6% of silica (80,96/20,57) show the best strength/reliability ratio.

4. Conclusions

– Reactions between reinforcement and base material produce an increase in sintering behaviour, due to reactions between the reinforcements and the white clinker that have an important influence on the mechanical properties and Weibull modulus.

– Silica is the additive that provides the greatest bending strength, due to the increase of belitic phase. Alumina addition also produces a strengthening.

– All composite materials present a Weibull modulus higher that of conventional ceramic, reaching a maximum value of 26,8 for white clinker reinforced with 9% of alumina. All composite materials show a Weibull modulus above 15. White clinker reinforced with 6% of alumina (86,23/22,35) and with 6% of silica (80,96/20,57) show the best ratio strength/reliability. The correlation coefficients of all materials over 95%.

– This work predicts different structural applications for these materials on account of their reliability, and the use of this process with different clinkers and other additives. It suggests greater expectations for these materials.

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