

## Suspension systems for coagulation processing

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New methods of ceramic processing based on colloidal processing are becoming increasingly important for advanced ceramic materials and in particular for complex shape components. Gel casting and Direct Coagulation Casting (DCC) represent the latest improvements in this area. These methods consist in consolidating a suspension with a high solid loading (>50% vol) in a non porous mould in order to obtain a green body with a very low shrinkage. The difference between the two techniques concerns the destabilisation mode. Our research team has chosen to develop the DCC process because it uses water as a solvent and the low content of organic additives in the suspension does not require a debinding stage. The main disadvantage is the low strength of green parts. A high state of oxides particle dispersion, in a pH range where no solubility of the particles occurs, was achieved by using an anionic electrolyte, Tiron,  $4,5(\text{HO})_2\text{C}_6\text{H}_2,1,3(\text{SO}_3\text{Na})_2$ . Its strong adsorption around the ZPC of the powder via the alcohol group creates a high repulsive potential between the particles via the  $\text{SO}_3^-$  groups. As this anion complexes efficiently a lot of ions in water, it shows a high affinity for the surface of the linked oxides, for example,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ . The coagulation of oxide/Tiron systems can be effective with the addition into the suspension of an aluminum salt, the Hydroxyaluminum diacetate,  $(\text{CH}_3\text{CO}_2)_2\text{AlOH}$ , whose decomposition in water can be controlled with the temperature value. The releasing of aluminum ions induces the pH decrease, the increase of the ionic strength and the dispersant desorption which are beneficial to destabilize the suspension.

**Key words:** dispersion, formulation, coagulation, suspensions, oxides.

### Introduction

The study of suspensions and in particular the dispersion of powders in aqueous and organic media constitutes the main topic of the research work developed by the team, from SPCTS laboratory in Limoges, France, specializing in the area of ceramic processing. The goal of this fundamental research, based on the determination of the key parameters which control the suspensions stability is to use new organic additives as dispersants or as binders to improve well known processes such as tape casting [1] or electrophoretic deposition and to develop new processes such as coagulation casting [2] or stereolithography [3].

Consolidation of colloidal suspensions into dense and homogeneous green bodies is a central feature of colloidal processing. Solidification can be induced via fluid removal, particle compaction or destabilisation without fluid removal. Concerning the last consolidation mechanism, the transition from a liquid, (the stable suspension), to a solid state, (the green body), occurs in the absence of liquid removal. Two of these forming routes, gel casting and Direct Coagulation Casting (DCC) can be compared. A concentrated colloidal suspension is required for the two processes.

The ceramic powder is dispersed only in water for DCC and in a monomeric solution for gel casting. After the deagglomeration stage and the suspension casting into a non porous mold, the organic compound which induces the consolidation is added. For gel casting, the addition of initiator catalyst leads to the gelation in situ of the solvent. The as-formed organic network encapsulates the ceramic particles, imparting high green strength. The first systems [4] used to develop this technique contained additives with high toxicity and new systems [5] are now being studied to overcome this problem. DCC relies on physical gelation of colloidal particles, as opposed to organic network formation in gelcasting. The suspension is destabilized by a time-delayed reaction, controlled by addition of a coagulation agent. With a high solid concentration, no linear shrinkage occurs during the liquid/solid transition and the drying of green body. The inherent advantage of this approach includes minimal binder content and no debinding stage is required. The Gauckler team, from Switzerland, showed the potentialities of this technique [6, 7]. Powder dispersion was achieved by creating a high repulsive potential between the particles thanks to the protonation or deprotonation of hydroxyl surface groups and the suspension coagulation was obtained by the decomposition of urea catalysed by an enzyme.

In our laboratory, the goal was to develop new systems for DCC, firstly to achieve a high state of particle dispersion with limiting powder solubility and

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**Table 1.** Main characteristics of powders

	Reference and purity	Size distribution d50 ( $\mu\text{m}$ )*	Specific surface area ( $\text{m}^2\cdot\text{g}^{-1}$ )**	Supplier
$\alpha\text{Al}_2\text{O}_3$	AKP30, >99.99%	0.35	7	Sumitomo, Japan
$\text{TiO}_2$ rutile	TRHP2, >99.7%	0.48	7	Bayer, Germany
$\text{ZrO}_2$	TZ3YS	0.40	5.5	Tosoh, Japan

\*Sedigraph 5100, Micromeritics; \*\* $\text{N}_2$  BET

secondly to control the transition liquid/solid via the kinetic and mode of coagulation because the means of destabilizing influences the coagulation time and therefore the green part cohesion. To obtain a stable suspension with high solid loading, an efficient dispersant must be used. In this work, an electrolyte derived from the catechol molecule (1,2-( $\text{HO}$ ) $_2\text{C}_6\text{H}_4$ ), Tiron (4,5-( $\text{HO}$ ) $_2\text{C}_6\text{H}_2$ -1,3-( $\text{SO}_3\text{Na}$ ) $_2$ ) was used. It is an efficient complexing agent of several cations such as  $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zr}^{4+}$  etc.... And this property enhances its adsorption onto particle surfaces of the corresponding oxide. This paper describes the dispersion mechanism of Tiron which was determined by using three oxide powders ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ). DCC was carried out to fabricate green bodies with alumina and zirconia as raw materials. Adsorption measurements and electrokinetic mobility of the suspensions provide useful methods to characterize the dispersion and coagulation of suspensions.

## Experimental procedure

The main features of the powders used in this study are summarized in table 1 and the commercial reagents were supplied by Aldrich.

### Adsorption

Tiron adsorption was measured versus pH for a fixed amount of Tiron per square meter of powder added. The solvent was an aqueous solution of NaCl ( $10^{-2}$  mol $\cdot\text{l}^{-1}$ ) used to fix the ionic strength and the pH was adjusted by using HCl and NaOH solutions; it remained constant during the adsorption period. The way to analyse the supernatant content has been described previously [2]. Table 2 summarizes the content of suspensions used.

### Zeta potential experiments

Zeta potential values of particles in the various slurries were measured using an electrokinetic sonic amplitude (ESA) measurement apparatus (Model ESA8000 Matec, Northborough, MA). This technique and its operating

**Table 2.** Content of suspensions for adsorption measurements

Oxide suspension	Solid concentration	Tiron concentration
$\alpha\text{Al}_2\text{O}_3$	3 vol%	$1.3 \times 10^{-6}$ mol $\cdot\text{m}^{-2}$
$\text{TiO}_2$	3 vol%	$1.3 \times 10^{-6}$ mol $\cdot\text{m}^{-2}$
$\text{ZrO}_2$	2 vol%	$1.1 \times 10^{-6}$ mol $\cdot\text{m}^{-2}$

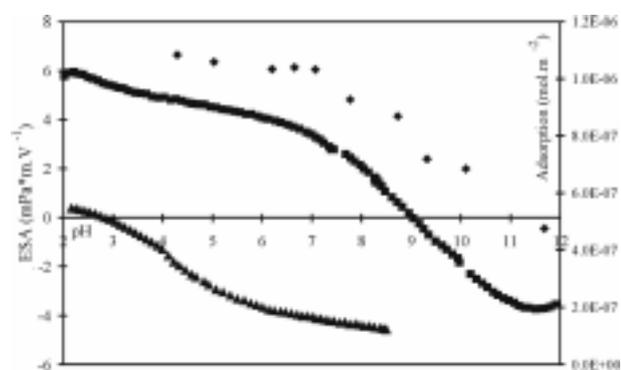
principles have been described previously. Measurements versus pH were carried out with slurries containing a 3.3 vol% solid loading. To measure the zeta potential values over a large pH range, two suspensions were used, one from natural pH to acidic pH and one more basic. The data recorded with the ESA analyser correspond to the measured ultrasonic signal converted to a voltage (ESA). The ESA data being directly proportional to the particles electrophoretic mobility [6], the electrokinetic properties variations versus pH will be presented using ESA values.

## Results and Discussion

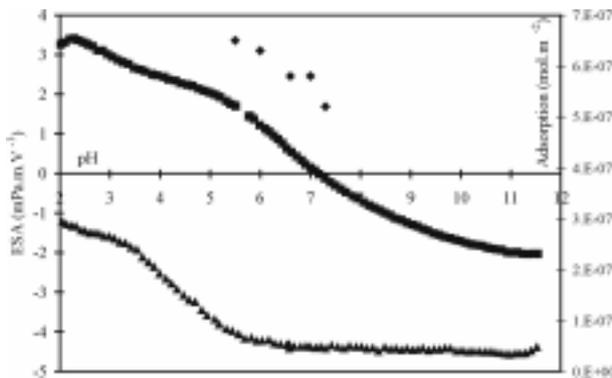
### Dispersion with Tiron

Figures 1, 2, 3 represent the electrokinetic properties of aqueous oxide suspensions versus pH and the amount of Tiron adsorbed is shown in the same figures.

Alumina powder has the higher ZPC (Fig. 1), as a powder with high purity has been used, a value of 9 was measured. A high repulsive potential can be created in acidic media (ESA =  $5.5 \text{ mPa}\cdot\text{m}\cdot\text{V}^{-1}$  at pH 3) but particle solubility induces the suspension ageing. Tiron addition into the suspension does not influence the natural pH of the suspension around 9 but its adsorption onto alumina particles leads to a high negative surface charge (ESA =  $-4.8 \text{ mPa}\cdot\text{m}\cdot\text{V}^{-1}$  at pH 9) which gives this molecule the ability to disperse alumina without a great shift of pH, preventing alumina solubility. As the pH becomes acidic, the negative charge decreases to reach the IEP at a pH value of 3. From pH 4, the surface charge varies linearly. With the



**Fig. 1.** Tiron, ( $\text{HO}$ ) $_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2\text{H}_2\text{O}$  adsorption ( $\blacklozenge$ ) versus pH onto AKP30 alumina surface. ESA data versus pH for an alumina suspension ( $\blacksquare$ ) with no additive, ( $\blacktriangle$ ) with  $1.3 \times 10^{-6}$  mol $\cdot\text{m}^{-2}$  of Tiron.



**Fig. 2.** Tiron,  $(\text{HO})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2\text{H}_2\text{O}$  adsorption ( $\blacklozenge$ ) versus pH onto TZ3YS zirconia surfaces. ESA data versus pH for an alumina suspension ( $\blacksquare$ ) with no additive, ( $\blacktriangle$ ) with  $1.1 \times 10^{-6} \text{ mol}\cdot\text{m}^{-2}$  of Tiron.

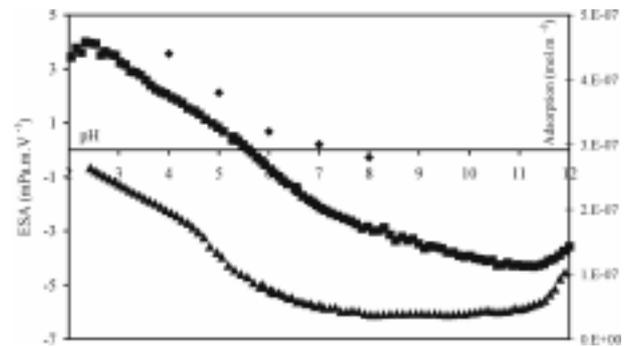
AKP30 powder, a suspension suitable for casting can be prepared with a solid concentration of 58 vol%.

By considering Tiron adsorption versus pH, we can see that an acidic media enhances its adsorption because of electrostatic attraction between the positive surface, due to the protonation of hydroxyl surface groups, and the anion. But in basic media, for  $\text{pH} < 9$ , electrostatic repulsion prevents dispersant adsorption.

Tiron was tested to disperse zirconia powder with a ZPC lower than that of alumina. The Fig. 2 shows that with the TZ3YS powder reference, ZPC is measured at a value of 7. With Tiron addition, a high negative surface charge is measured from pH 6.5 to 11. For pH lower than 6.5, the amplitude of the negative surface charge decreases because free hydroxyl groups are protonated and give a positive contribution to the surface charge. But by examining closely the curve, from pH 3.7, we see the decrease occurs more slowly and linearly indicating a change of interaction between powder surface and the electrolyte. With this Tiron concentration, which corresponds to the quantity which leads to the minimum in viscosity, no IEP is detected. A suspension with a solid concentration of 45vol% can be prepared.

Concerning adsorption data, as for the alumina powder, a positive surface ( $\text{pH} < \text{ZPC}$ ) enhances Tiron adsorption.

The data (Fig. 3) relative to titania powder, with a ZPC of 5.5 show the same tendency. A high state of dispersion can be achieved at a natural pH of 6.5 and a



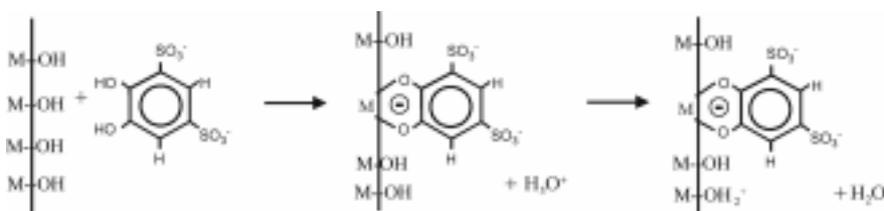
**Fig. 3.** Tiron,  $(\text{HO})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2\text{H}_2\text{O}$  adsorption ( $\blacklozenge$ ) versus pH onto TRHP2 titania surfaces. ESA data versus pH for an alumina suspension ( $\blacksquare$ ) with no additive, ( $\blacktriangle$ ) with  $1.3 \times 10^{-6} \text{ mol}\cdot\text{m}^{-2}$  of Tiron.

suspension with a solid concentration of 62 vol% can be cast. And as acidic media ( $\text{pH} < \text{ZPC}$ ) enhances Tiron adsorption, the negative surface charge decreases linearly and no IEP is detected with this Tiron concentration.

According to the electrokinetic properties of these three powders with different ZPC, some hypotheses have been made about interactions between Tiron and powder surfaces versus pH.

Around ZPC, a majority of hydroxyl groups are neutral and Tiron adsorption should occur *via* the formation of an inner sphere complex as shown in Fig. 4. A ligand exchange between the OH surface group and the anion via alcohol functions leads to a strong adsorption and ionized  $\text{SO}_3^-$  functions to an excess of negative surface charge creating a high repulsive potential between the particles. From the ZPC, as the pH decreases, OH groups are protonated and when the concentration of  $\text{OH}_2^+$  becomes sufficient, the anion is electrostatically attracted by the surface and adsorption should occur as an outer sphere complex (Fig. 5) via  $\text{SO}_3^-$  groups. This Tiron configuration onto the powder surface leads to the neutralization of  $\text{OH}_2^+$  groups and is expressed as a linear variation of electrokinetic properties in acidic media.

To conclude this discussion about dispersion, the Tiron molecule permits the systems to achieve a high state of dispersion in aqueous media for several oxides. This dispersant has been successfully tested with  $\text{GeO}_2$  and  $\text{Sb}_2\text{O}_5$  powders but we can note that this molecule does not complex the silicon cation so then powders



**Fig. 4.** Inner sphere complex between Tiron and oxide surface.

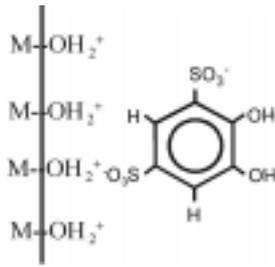


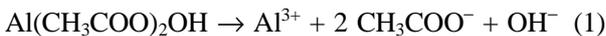
Fig. 5. Outer sphere complex between Tiron and oxide surface.

based on silicon can not be dispersed with Tiron.

### Coagulation of suspensions dispersed with Tiron

After the preparation of a stable suspension with a high solid loading, the second step of the DCC process which leads to the suspension consolidation is coagulation. A stable system can be flocculated either by shifting the suspension pH near the IEP to strongly reduce the total interaction potential between particles, by increasing the ionic strength to compress the electrical diffuse double layer, or by desorbing the dispersant to diminish the repulsive potential. Moreover the kinetics of the reaction which induces coagulation must be controlled to have enough time to cast the suspension.

To coagulate an alumina suspension dispersed with Tiron, a salt of aluminum, hydroxyaluminum diacetate  $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$  has been used. This powder, almost insoluble in water, decomposes itself as the temperature increases to release  $\text{Al}^{3+}$  and acetate ions (eq. 1).



After the sintering stage (1600°C), this compound

leads to  $\alpha\text{-Al}_2\text{O}_3$  and brings no impurities. As alumina is a sintering additive for zirconia, the coagulation agent was tested to destabilize alumina and zirconia suspensions dispersed with Tiron.

To study the transition from a stable to a flocculated system, rheological measurements with an oscillatory mode were carried out. These measurements were performed under small deformations in the linear viscoelastic domain and permitted one to determine the optimum concentration of  $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$  and the coagulation temperature. Results were presented and discussed in a previous paper [2] and it was shown that the hydroxyaluminum diacetate is an efficient coagulation agent for the alumina and zirconia systems.

By following electrokinetic properties of suspensions, we can determine the parameters which induce the suspension destabilisation. The pH, ionic conductivity and surface charge density were measured versus time at 35°C for alumina and zirconia suspensions dispersed with Tiron, in which  $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$  was added at  $t = 0$  min (Figs. 6 and 7). The addition of the coagulation agent influences in the same way the three parameters measured, whatever the system studied. The natural suspension pH strongly decreases just after the flocculant addition to reach a minimum value around 4.5, which is the pKa of acetic acid. Up to two hours of measurements, this value remains constant, but zirconia solubility should allow a slow increase in the pH. The  $\text{Al}^{3+}$  ions released, precipitate as  $\text{Al}(\text{OH})_3$  leading to a rapid pH decrease. This pH variation allows a shift of the pH near the IEP, reducing the interaction potential between particles and at the same time, the suspension becomes very thick. At pH 4.5, the aluminum ions released contribute to increase gradually the ionic conductivity into the suspension and then the ionic

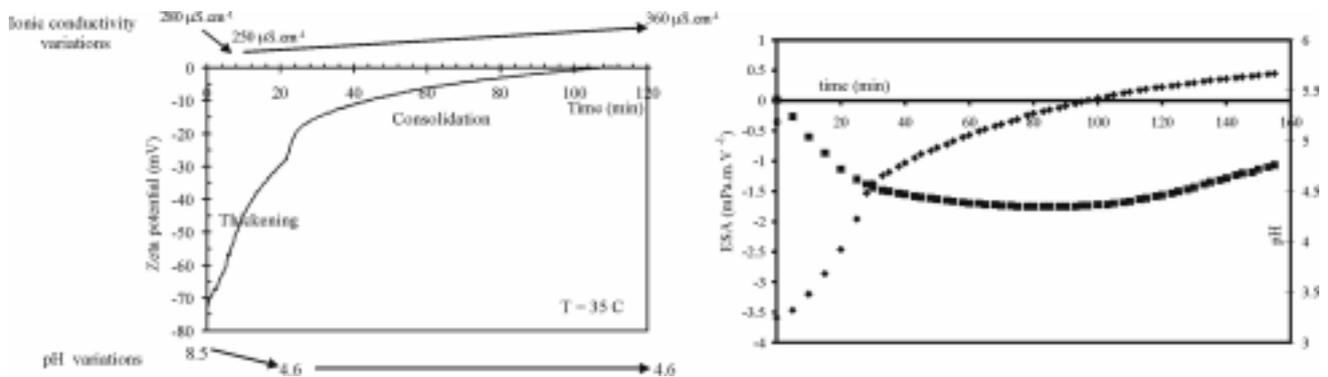
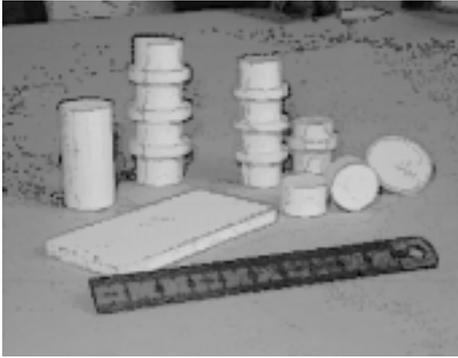


Fig. 6 and 7. Electrokinetic properties of alumina and zirconia suspensions during the coagulation stage.

Table 3. Suspensions content for DCC

Raw material Suspension concentration	Tiron concentration	$\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$ Concentration (mole per liter of solvent)	Temperature Coagulation time
$\text{Al}_2\text{O}_3$ , 58 vol%	$1.3 \times 10^{-6} \text{ mol}\cdot\text{m}^{-2}$	0.43	60°C, 2 hours
$\text{ZrO}_2$ , 45 vol%	$8.2 \times 10^{-7} \text{ mol}\cdot\text{m}^{-2}$	0.15	60°C, 2 hours



**Fig. 8.** Alumina parts fabricated by DCC.

strength. The zeta potential values decrease slowly to reach the value of 0, the suspension becomes cohesive and the part can be demolded. As  $Al^{3+}$  ions are produced into the suspension, Tiron desorption occurs enhancing the suspension destabilization [2]. Internal coagulation was mainly due to the  $Al^{3+}$  ions release. In this form, this is a new variation of internal coagulation.

To validate this processing route, complex-shaped components with large and small cross sections have been fabricated (Fig. 8). Table 3 summarizes the experimental conditions to carry out DCC with alumina and zirconia powders.

We can note that as alumina is a sintering additive of  $Si_3N_4$ ,  $Al(CH_3COO)_2OH$  could be used as a flocculating agent to carry out DCC processing of  $Si_3N_4$  parts.

## Future

Concerning the perspectives of this work, fundamental research will be developed through a project between two French laboratories. The goal of this project is to determine the organization of particle networks during the coagulation stage. Other systems will be developed with other coagulation agents, because the mode and the kinetics of coagulation influence the structure of the particle networks, and then the green part cohesion. Atomic force microscopy and diffusion wave spectroscopy techniques linked to electrokinetic and rheological properties of suspensions should permit us to achieve this goal.

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