

INFLUENCE OF AN ULTRASONIC TREATMENT ON THE STRUCTURE AND FLOW BEHAVIOUR OF OXIDE CERAMIC MASSES

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ABSTRACT:

Oxide ceramic masses are used for catalysts and catalyst carriers. For a reliable processing hydrocolloids (e. g. cellulose) are usually added in order to decelerate demixing phenomena. Oxide ceramic masses react to simple shearing with hardening (peptisation: increase of the shear stress with the shear deformation) [1]. The present study analyses, if an ultrasonic treatment has also an impact on the structure, the shelf-life (in the green state), the correlated flow behaviour of oxide ceramic masses and presumably (not tested) the mechanical properties in the hardened, sintered state. The idea of using ultrasonic treatment is to change the microstructure (see below) and, therefore, to minimise or even give up the standard addition of stabilizers to minimize demixing in aqueous oxide ceramic suspensions. Besides the additional costs of an extra process unit, stabilisers cause often deteriorated mechanical properties (porosity, crack behaviour) of the ceramics in the hardened state after the sintering. Therefore, pump experiments (apparent viscosity), oscillatory (G' and G'') and steady shear experiments (h), particle-size analysis (particle-size distribution, agglomerate strength), light microscopy, decanting experiments and pH-determinations have been performed. The obtained results show, that the hardening of the apparent viscosity (derived from the flow) during pump experiments with simultaneous ultrasonic treatment in a flow cell is combined with an increase of the fine fraction, the formation of enlarged, but smoother agglomerates, the change of the pH-value and the evolution of a three-dimensional network (gelling). All these processes increase both the amount of bound/immobilised (chemically or physically bound by or onto the solid-surfaces) and of retained water (interior of agglomerates and/or the pores of the flowand ultrasonic-induced network). This means that the volume fraction of the rheologically "free" water decreases and simultaneously the effective solid volume fraction increases. With respect to the concept of the rheologically effective solid fraction this is combined with an increasing viscosity. At the same time the tendency of demixing decreases significantly. Thus, by an appropriate combination of shear flow and ultrasonic treatment, the aqueous oxide ceramic suspensions are stabilised and a reliable processing of the initially problematic solid/fluid mixtures can be realised without stabilisers (eluding their negative consequences with respect to the quality of the sintered state).

ZUSAMMENFASSUNG:

Keramikoxide werden für Katalysatoren und Katalysatorträger benötigt. Für eine zuverlässige Verarbeitung werden Hydrokolloide (z. B. Zellulose) üblicherweise hinzugefügt, um Entmischungsphänomene zu verlangsamen. Keramikoxide reagieren auf einfache Scherung mit Verfestigung (Peptisation: Erhöhung der Scherspannung mit der Scherdeformation) [1]. Die vorliegende Arbeit untersucht, ob eine Ultraschallbehandlung auch eine Auswirkung auf die Struktur, die Haltbarkeit (im grünen Zustand), das korrelierte Fliessverhalten von Keramikoxiden und eventuell (nicht getestet) den mechanischen Eigenschaften in dem gehärteten, gesintertem Stadium hat. Die Idee, die Ultraschallbehandlung zu verwenden, ist, die Mikrostruktur (siehe unten) zu verändern und deshalb die übliche Zugabe von Stabilisatoren, um die Entmischung in wässrigen Keramikoxidsuspensionen zu vermindern, zu reduzieren oder gar zu unterdrücken. Neben den zusätzlichen Kosten einer weiteren Prozessseinheit verursachen Stabilisatoren häufig verminderte mechanische Eigenschaften (Porosität, Rissverhalten) der Keramiken in dem gehärteten Zustand nach dem Sintern. Daher wurden Pumpexperimente (scheinbare Viskosität), oszillatorische (G' und G'') und stationäre Scherexperimente (h), Partikelgrößenanalyse (h) (Partikelgrößenverteilung, Agglomerationsstärke), Lichtmikroskopie, Dekantierexperimente und pH-Wertbestimmungen durchgeführt. Die erhaltenen Resultate zeigen, dass die Verfestigung der scheinbaren Viskosität (die vom Fliesen gewonnen wurde) während der Pumpexperimente mit gleichzeitiger Ultraschallbehandlung in einer Fließzelle verbunden ist mit dem Ansteigen der feinen Fraktion, der Bildung grösserer, dafür aber glatterer Agglomerate, der Änderung des pH-Wertes und der Bildung eines dreidimensionalen Netzwerkes (Gelierung). Alle diese Prozesse erhöhen den Betrag der gebundenen/immobilisierten (chemisch oder physikalisch gebunden durch oder auf den festen Oberflächen) und des zurückgehaltenen Wassers (innerhalb der Agglomerate und/oder der Poren des Fließ- und Ultraschallinduzierten Netzwerkes). Dies bedeutet, dass der Volumenanteil des rheologisch "freien" Wassers abnimmt und gleichzeitig der effektive Festkörpergehalt zunimmt. Mit Bezug auf das Konzept des rheologisch effektiven Festkörpergehaltes ist dies mit einer erhöhten Viskosität verbunden. Gleichzeitig sinkt die Tendenz zur Entmischung signifikant. Daher können durch eine angemessene Kombination einer Scherströmung und einer Ultraschallbehandlung die wässrigen Keramikoxid-

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For the chosen experimental set-up air, which (i) is present in the sample during and after the preparation and which (ii) is entrained into the sample in the storage vessel may have various effects on the energy input and the structure and flow-behaviour of the samples. The included air enhances the attenuation of ultrasonic in the treated material and causes a decrease of the fraction of actual treated material. On the other hand, the air bubbles and the dissolved air facilitates the occurring of cavitation. It is difficult for the time being to decide which effect dominates. Problematic is also the continuous recirculation of the suspension. This set-up guarantees that the fluid is homogeneously treated with ultrasonic independent on the instantaneous consistency and composition. Ultrasonic experiment with a stirring vessel showed that after the gelling had appeared, only regions of the material next to the sonotrode were ultrasonic treated. The rest of the sample was at rest, since the stirrer was not able to overcome the yield stress of the sample in the whole vessel. A strong negative aspect of the flowcell is that the impact of flow- and ultrasonic-induced phenomena on the structure and flow-behaviour are hard to separate. Preliminary tests show that samples ultrasonic-treated in a vessel with moving sonotrode (Fig. 10) show a better syneresis behaviour and a better long-term stability compared to samples treated in the flow-cell. This might be a hint that structures in the samples, which are appropriate to immobilise water are destroyed by the flow process.

Possible superior aims of an ultrasonic treatment are to achieve a stable mixture (at least during the processing) with a minimum of ultrasonic energy input and treatment duration and a viscosity η_{app} as low as possible. Thus, the energy input and the abrasion of the production-devices, i.e the acquisition and maintenance costs might be minimised. The variation of the solid-concentration and also of the temperature and the ultrasonic power input seems to be a promising approach to optimise the structure in combination with the flow-behaviour of ultrasonic-treated disperse systems. Further interesting influencing parameter are surface energies which could be modified by variation of the pH-value and addition of appropriate ions. By an appropriate combination of flow and ultrasonic treatment an reliable processing of the initially

problematic solid/fluid mixtures could be realised on an industrial scale.

There is still a lot of fundamental research to be done for a deeper understanding of the processes involved during the ultrasonic treatment of disperse solid-liquid systems and the complex interplay between composition, structure, process units, and process parameters. Online measuring techniques are required, which are capable to detect and monitor structural changes in the interior of the disperse systems and which do not require to interrupt the process or to prepare the samples.

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