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Suivi en-ligne des procédés de cristallisation en solution en milieux pur et impur par émission acoustique

Acoustic On-line monitoring of solution crystallization process in pure and impure media

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Résumé

De nombreux processus mécaniques et physiques s'accompagnent de la génération d'ondes acoustiques dues à une libération rapide et localisée d'énergie au sein des matériaux. L'acquisition et le traitement de ces ondes permet un contrôle non-destructif de nombreux phénomènes tels que la fissuration sous contrainte, la déformation élastique, le changement de phase, etc. Peu de travaux ont été consacrés par le passé à l'émission acoustique (EA) pendant les procédés de cristallisation et l'essentiel des travaux disponibles, purement descriptif, ne fournit pas de résultats susceptibles de permettre une évaluation quantitative indirecte des processus élémentaires de la cristallisation (i.e., nucléation, croissance, agglomération, etc.).

On présente ici des résultats nouveaux obtenus pendant le suivi de cristallisations discontinues en solution. Les signaux acoustiques recueillis sont interprétés grâce à la mesure, en parallèle, de la phase continue (mesure de concentration par spectroscopie ATR FTIR) et de la phase dispersée, par acquisition d'images de la suspension à l'aide d'une sonde vidéo *in situ*. On montre que les capteurs d'émission acoustique "perçoivent" le déroulement de la cristallisation et, en particulier, qu'elle permet une détection extrêmement précoce de la nucléation des cristaux. Une analyse des composantes des signaux acoustiques montre également que l'EA permet de suivre séparément plusieurs processus élémentaires de la cristallisation qui restent à identifier clairement. Les mesures ainsi obtenues ouvrent des perspectives prometteuses quant au suivi en-ligne des opérations de cristallisation industrielle.

Abstract

Many mechanical and physical processes are associated with the generation of acoustic waves produced by the rapid release of energy from localized sources within a material. Acquiring and processing these waves allows non-destructive control of phenomena such as the extension of cracks in a structure under stress, plastic deformation, phase transitions, etc. Few works were devoted in past to acoustic emission (AE) during crystallization processes. Moreover, most available studies are purely descriptive and do not provide results enabling to quantitatively monitor basic crystallization phenomena (i.e., nucleation, growth, agglomeration, etc.)

New results dealing with the monitoring of batch solution crystallization operations are presented here. The acquired acoustic signals are interpreted thanks to the joint monitoring of the continuous phase (Measurement of the solute concentration thanks to ATR FTIR spectroscopy) and of the dispersed phase, thanks to the video in situ acquisition of images of crystals in suspension. It is shown that acoustic emission sensors "perceive" the development of the crystallization process and, in particular, that an early detection of the nucleation of crystals is allowed. Analysing the parameters of acoustic waves is shown to allow separate monitoring of basic crystallization phenomena which remain to be identified. As far as on-line monitoring of industrial crystallization processes is concerned, the measurements thus obtained open promising perspectives.

Mots-clés : Cristallisation industrielle, capteurs, émission acoustique, acquisition d'images.

Key-words : Industrial crystallization, sensors, acoustic emission, image acquisition.

1. Introduction

Acoustic Emission refers to the generation of transient elastic waves during the rapid release of energy from localized sources within a material. The source of these emissions is closely associated with movements accompanying plastic deformation and with the initiation and extension of cracks in a structure under stress. Many physical phenomena generate acoustic emission: melting, phase transformation, thermal stresses cool down cracking and stress build up. This is why acoustic emission (AE) testing is one of the most interesting techniques used for the non-destructive evaluation of materials as it has shown its ability to monitor changes in materials behavior over a long time. For example, the technique has long been used in material sciences to detect crack propagations occurring not only on the surface but also deep inside a material. Many successful AE applications in engineering were reported in the past for a broad variety of materials, material compositions and structures (Stephens 1968), but few studies were devoted to applications of the technique in crystallization and, among these studies, a very limited dealt with quantitative monitoring of crystallization systems. However, AE has been used for a number of applications in the pharmaceutical industry for monitoring various chemical engineering processes (W.R. Boyd & Varley 2001) including fluidized bed granulation (Matero et al. 2010), fluidized bed coating (Naelapää et al. 2007), powder compaction (Hakanen & Laine 1993).

The objective of this work is to evaluate the potential for using acoustic emission to monitor polythermal batch crystallization in the absence and presence of impurities. The basic concept behind AE monitoring of batch crystallization is that the phase transition occurring during crystallization in solution induces physicochemical changes in the suspension that release energy and generate acoustic elastic waves propagating in the medium (Garten & Head 1966). Furthermore, when particles are generated, the elastic properties of the dispersed phase also change. These changes affect the acoustic emission caused by the particle collision impacts and inter-particles and/or particles-wall frictions. The elasticity of crystals and their kinetic energy are also affected by many other properties such as size, shape, hardness, density, uniformity of composition which all obviously depend on the presence of impurities in the medium.

We report preliminary batch solution cooling experiments obtained with the model system Ammonium Oxalate/water in the presence of low Nickel Sulfate amounts as impurity.

Two different studies were carried out. The first study aimed at understanding the origins of the different acoustic signals emitted during the polythermal crystallization of ammonium oxalate aqueous solutions. It is also aimed at demonstrating the ability of AE technique to detect changes in physico-chemical properties of liquid and dispersed phases during crystallization by comparing the collected signals to the development of crystallization steps and phenomena (nucleation, growth, breakage) which, in addition, are mathematically predicted using Population Balance Equation (PBE) models (Févotte & Févotte 2010)

The purpose of the second study is to establish to which extend acoustic emission technique can provide valuable information about the effect of nickel sulfate impurities on the development of the crystallization process. Indeed it is clear that basic crystallization kinetics and crystals morphology are affected by impurities present in the suspension and to date, despite the tremendous industrial importance of impurities, no successful study relating acoustic activity and effect of impurities on crystal nucleation and growth morphology is reported (Cook et al. 1993).

2. Experimental design

A 3 L glass vessel equipped with a jacket and a condenser was used for the experiments. The bench-scale plant presented in Fig.1 plant was instrumented and computer-controlled to allow tracking set-point temperature trajectories. Cooling was performed by means of heat transfer through the jacket wall: the temperature was controlled by manipulating automatically the set-point temperature of a heating bath containing water and glycol.

I*n situ* concentration measurements were performed using the infrared spectrometer "MATRIX-F" manufactured by Brucker Optik GmbH, equipped with ATR-diamond immersion probe. The acquisition of the IR spectra was performed to yield measurements of solute concentration. The calibration method was presented in many papers and will not be recalled here (Gherras & Févotte 2011a-b). After validation, the calibration model was firstly used to evaluate the time variations of supersaturation, as displayed in Fig.2.

In addition to in situ FTIR measurement of solute concentration, the CSD of the final product was measured through image analysis, using the "EZProbe" (Presles et al. 2010), an in-situ imaging probe developed at the University Lyon 1. The imaging probe allowed real time acquisition of 2D images of AO particles during the batch process, as shown in Fig.3. Size measurements were then performed for each discernible crystal, with a minimum sample of 900 crystals per CSD analysis. Due to the time required by the processing of the video pictures, few CSD were actually evaluated for each experiment.

An acoustic piezo-electric sensor was stuck on the jacket wall and connected to the acoustic emission testing device.

The AE experimental set up consists of an AEDSP 32/16 MISTRAL digital system from Physical Acoustics Corporation. This system makes it possible to record the waveforms and the main AE parameters such as AE absolute energy, counts, amplitude and duration.

The sampling rate was 4MHz. A piezoelectric test sensor (nano 30) with a frequency resonance of 300 KHz was connected to the vessel wall through 40 dB preamplifier and a frequency filter (20 to 1200 KHz). A coupling fluid was used to have an airless and flawless contact between the transducer and the vessel wall. The acquisition parameters PDT (peak definition time), HDT (hit definition time) and HLT (hit lockout time) were 10, 10 and 20 µs, respectively.

This sensor has already been used as a reference sensor in order to record noises due to the electromagnetic environment, the flow pattern of the heated and agitated supersaturated ammonium oxalate solutions and the flow pattern of the cooling fluid through the jacket wall, in order to fix an operational threshold for EA measurements (AE absolute energy reference value is about 600 atto Joules ($600 \cdot 10^{-9}$ J) and the AE amplitude acquisition threshold is 30 dB).
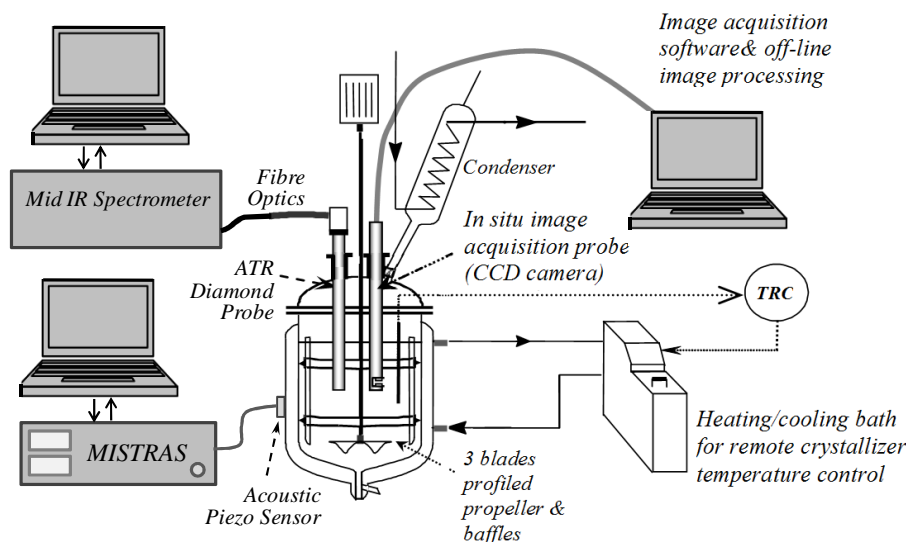

Figure 1. Schematic of the lab-scale crystallization plant equipped with ATR FTIR measurement of solute concentration, in situ imaging probe and acoustic emission testing device.

AO undersaturated solutions were prepared by dissolving appropriate amounts of analytical grade ammonium oxalate monohydrate in 1800 ml water. The initial AO concentration was 0.1 kg/kg solvent. Linear cooling experiments were then carried out at varying linear cooling rates, namely: 2, 5, 7, 10, 12, 20, 25 and 30 °C/h. The cooling procedure was stopped at 293K and followed by a period of stabilization of 3 hours at this latter temperature. Suspension samples were then withdrawn at 293K, filtered off and dried for optical microscopy and SEM investigation.

3. Main experimental results

Thanks to the AE monitoring of the batch cooling crystallization processes, primary nucleation was very early detected, much before the end of the so-called induction period. Figure 2 shows the time variations of the acoustic absolute energy emitted during the crystallization process. A plot of the measured supersaturation profiles is also displayed on the same figure. As a result of the cooling process, the relative supersaturation σ increases until a sharp peak (for σ=0,15) where it suddenly decreases. The tip of the peak corresponds to the onset of primary nucleation. Figure 2 also shows pictures of the suspension which were taken during the development of the batch process: it can be seen that few crystals are in suspension (Picture B) much before reaching the limit of metastable zone. This observation is not surprising as the dynamic model of the crystallization predicts that crystals are generated as soon as the system becomes supersaturated, even though the amount of solid produced is not yet enough to yield significant solute consumption. Moreover, surprisingly, one can see that small acoustic events are detected much before (point A) any solid generation can be detected. This experimental observation is of special importance because it could means that AE allows monitoring the very early step of primary nucleation which.

Figure 3 displays the time variations of the rate of production of solid computed from the solute concentration measurements. The acoustic energy released divided by the corresponding solid produced, $(dE/dt).m_s^{-1}$ (right grid) is also plotted in Fig.3. It appears that $(dE/dt).m_s^{-1}$ increases very sharply 1-2 minutes before the starting of the nucleation peak. Again, in terms of solid production monitoring (left grid), it is clear that the acoustic emission is very efficient and sensitive, especially when compared with usual sensing techniques.
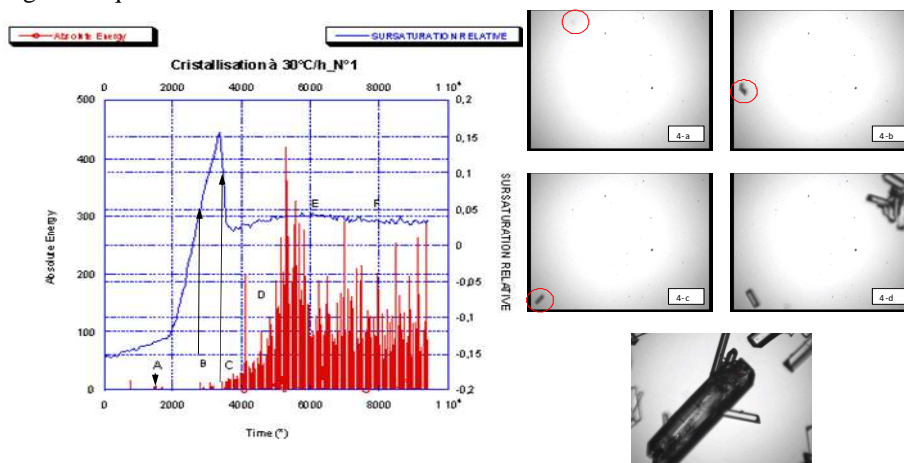

Figure 2. Batch cooling crystallization of ammonium oxalate: time variations of the solute concentration measured using ATR FTIR spectroscopy and absolute acoustic energy (normalized with respect to the mass of solids).

The effect of impurities on the acoustic emission of crystallizing slurries was also investigated in order to assess the possibility of evaluating the concentration of impurities in industrial mother liquors and, if possible, the detrimental effect of impurities of the properties of the final crystals. As one can see in Fig. 4, some very encouraging results were obtained. The most important and straightforward observation is the clear decrease of the overall energy for increasing impurity concentrations. It should be noticed that, parallel to the AE monitoring, it was observed though in situ image acquisition and further scanning emission microscopy that the crystals grown in the presence of impurities exhibit irregular, rough and broken shapes. Even though the incorporation of impurity species in the crystal lattice is not clearly proven in the present case, it is obvious that the mechanical properties of crystals grown in impure solvent are severely impaired. It is very likely that similar detrimental effects, and their indirect measurement through AE testing can be correlated and, therefore, can be used to estimate the in-line some key-properties of the solid product.
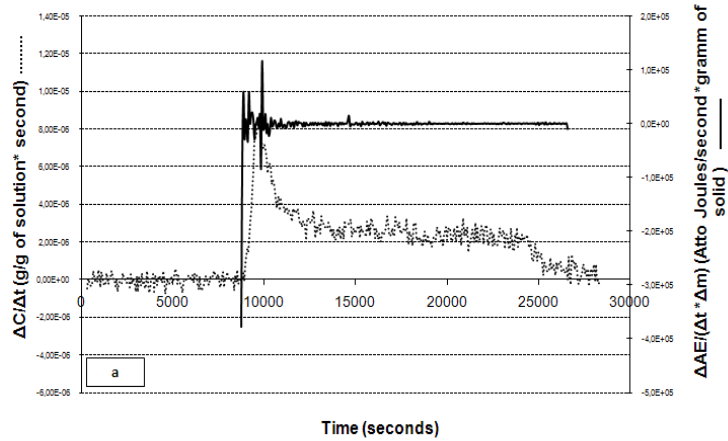
Figure 3. Time variations of the solid production rate dCs₅/dt computed from ATR FTIR spectroscopic measurements of concentration and absolute acoustic energy (normalized with respect to the mass of solids).
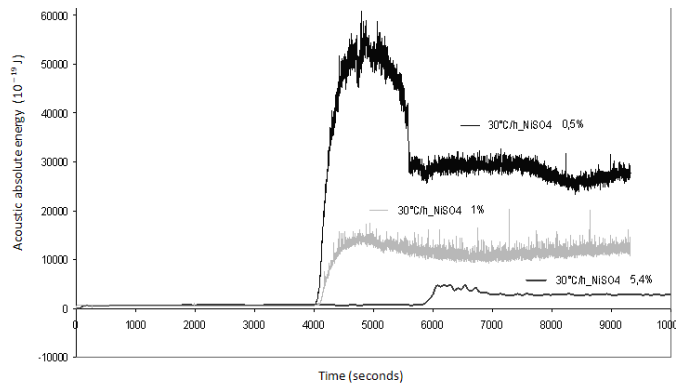

Figure 4. Time variations of absolute acoustic energy for varying impurity concentration (0.5; 1 and 5%) and constant cooling rate, dT/dt=-30°C/h.

Among the many acoustic parameters computed using EA softwares, several informative variables were identified as highly representative of the development of distinct basic crystallization phenomena. The processing of relevant acoustic signals emitted during crystallization in pure and impure medium and their comparison with experiments performed with glass beads of calibrated size showed a clear hindering effect of impurities on the growth of crystals and a promoting effect for the production (secondary nucleation and breakage) of smaller ones. From this latter point of view, typical examples displayed in Fig.5 are extremely interesting, even though the physics governing crystals AE remains to be explained. Roughly speaking, Fig.5 shows that the crystallization in pure water corresponds to the highest level of energy released (note that curve 1 is cut) associated to a phenomenon located in a very narrow cluster (1 in Fig.5A). Two distinct phenomena also take place during the process that both reach a steady state value. On the contrary, it is clear that not only the amount of impurities reduces the energy released by AE, but the dominant processes are not "located in the same clusters" (cluster 2 was negligible with pure medium while it dominates with 0.5% impurity content). It can be concluded the highest impurity concentration leads to different absolute energy profiles which all reach a steady-state before the end of the crystallization process. The results obtained with 5.5% impurity concentration is also remarkable by the fact that the process related to cluster 4 seems to be related to a new and dominating phenomenon that remains to be clearly identified.

It seems therefore reasonable to conclude that for industrial batch crystallization monitoring purposes, the AE technique, due to its many advantages (i.e., the sensor is passive, non intrusive, non destructive and cheap) is a promising tool for the assessment of impurities effects during industrial crystallization processes, the early detection of nucleation. One can also expect AE monitoring to provide new tools for monitoring and studying crystal nucleation and growth.
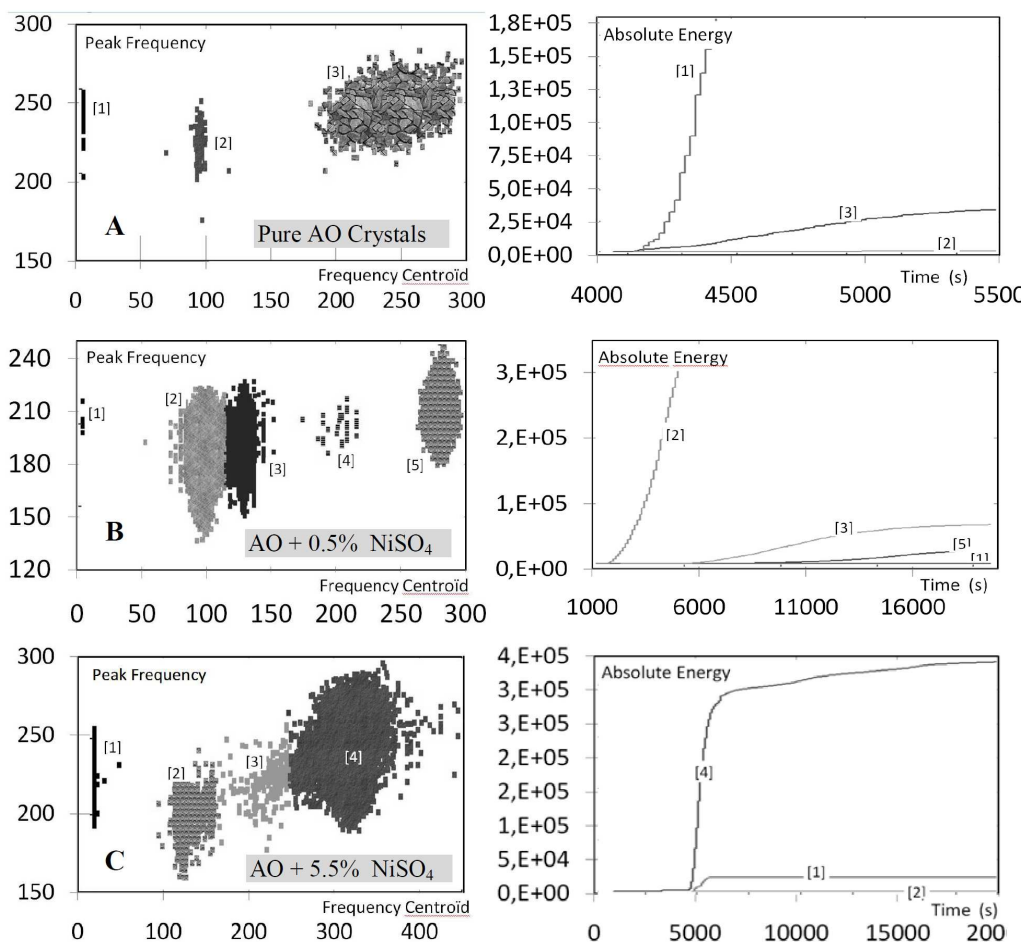
Figure 5. Clustering of acoustic variables and respective evolutions of the related energy during 3 batch processes. The 3 experiments were performed with dT/dt=-30°C/h

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