FACET

dutch association for crystal growth
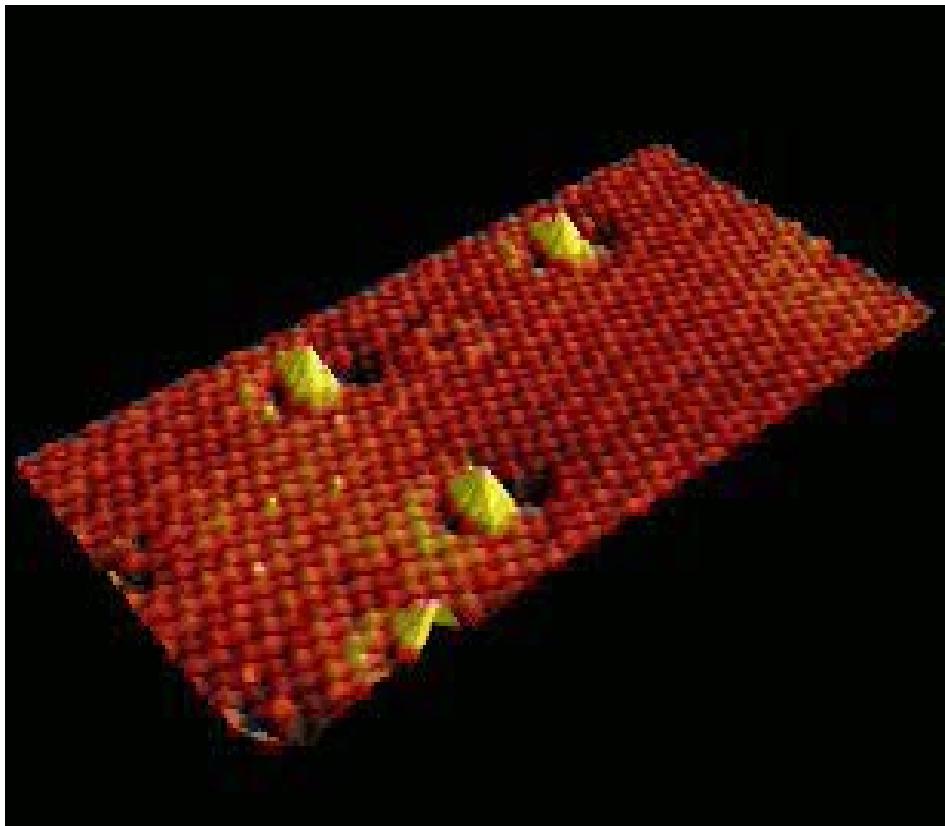
DACG

NVKG

nederlandse vereniging voor kristalgroei

i n f o r m a t i e b l a d   v a n   d e

3 november 2000 vervalt!

i n h o u d

Secretariaat NVKG

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Dr. A. van Geelen	lid
Prof. dr. J. van der Eerden	lid
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Omslagfoto

De voorkant laat een in situ Scanning Tunneling Microscope (STM) opname zien van het (001) oppervlak van koper kristal. Het regel-matige patroon van kleine bobbeltjes komt overeen met het atomaire rooster van koper-atomen. De grote bobbels zijn indiumatomen die bij kamertemperatuur in een vacuüm-systeem zijn opgedampt. Deze indiumatomen zijn spontaan naar binnen gediffundeerd in de buitenste atoomlaag van het koperkristal. Elk indiumatoom neemt de plaats in van één koperatoom. De indiumatomen zorgen er voor dat de groei van koper op dit oppervlak laag voor laag plaatsvindt, in plaats van in de vorm van ruwe, drie-dimensionale groei. De indium-atomen blijken zelf binnen de buitenste koper-laag een wonderlijke diffusiebeweging uit te voeren, waarbij ze 'reuzesprongen' maken van meerdere atoomafstanden. Dit blijkt het gevolg te zijn van de ultrasnelle diffusie van een uiterst lage dichtheid van oppervlaktevacatures (ontbrekende koperatomen in de buitenste laag).

Foto aangeleverd door: Raoul van Gastel en Joost Frenken, Universiteit Leiden

Redactioneel: roep om kiemen!

Voor u ligt de tweede FAC ET van dit jaar. In deze FAC ET vindt u de aankondiging van de jaarvergadering en de excursie bij de firma Uniphase in Eindhoven. Zoals u ziet vindt deze

bijeenkomst *niet* plaats op 3 november 2000, zoals werd aangekondigd in de vorige FACET, maar op vrijdag 12 januari 2001.
Opnieuw doet de redactie op deze plaats een 'emotionele' oproep naar input. Wat kunt u bijdragen?

- Aankondigingen van lezingen, symposia en congressen (niet alleen de activiteiten die u zelf organiseert, maar ook activiteiten waarover u langs andere weg geïnformeerd bent)
- Verslagen van (kristalgroei)-conferenties
- Artikelen (mag ook heel kort zijn!) over een opmerkelijke ontdekking
- Advertenties: bijvoorbeeld i.v.m. vacature
- Omslagfoto's (met toelichting). Telkens zal de beste ingezonden foto op de omslag van de FAC ET worden afgedrukt samen met een korte toelichting aan de binnenzijde van het blad. Bovendien zullen de foto's op de fotogalerij van onze webstek worden gepost: (http://www.kncv.nl/secties/kkn/index.html)

Zoals al eerder gemeld is de drempel voor uw bijdragen zeer laag: aanleveren kan per brief, fax, e-mail, of telefoon. En we staan natuurlijk open voor alle direct of indirect met de NVKG verwante onderwerpen.

Joost Frenken

Elektronisch

Deze FACET wordt opnieuw elektronisch verspreid. Vanaf nu gebeurt dat in de vorm van een PDF-file. Dit is het file-type dat probleemloos op elke computer kan worden gelezen. Hiervoor hebt u het programma Acrobat Reader nodig, dat *gratis* op uw computer wordt gezet vanaf de website van Adobe. Net zoals de vorige elektronische FACET, bevat ook dit exemplaar automatische links voor web en e-mail. Staat u nog niet op onze elektronische mailing-lijst, laat het ons dan even weten!

Excursie / algemene ledenvergadering
Vrijdag, 12 januari 2001, Uniphase, Eindhoven

Op vrijdag 12 januari 2001 organiseert Dr. A. van Geelen, van de firma Uniphase Netherlands B.V. in Eindhoven, de gecombineerde EXCURSIE / ALGEMENE LEDENVERGADERING.
Het lezingenprogramma is georganiseerd rondom het thema: *III-V Semiconductor: from niche applications to mainstream market*. Naast de lezingen wordt ook een rondleiding bij Uniphase verzorgd. Het lezingen- en rondleidingprogramma wordt gecombineerd met de algemene ledenvergadering (2000) van de NVKG.

PROGRAMMA EXCURSIE / ALGEMENE LEDENVERGADERING; *III-V Semiconductors*

09:30	ONTVANGST EN KOFFIE	
	Lezingenprogramma	
09:55	Welkomstwoord	A. van Geelen
10:00	Inleiding Uniphase en producten	P. Thijs
10:30	GaN groei voor LED's en hoogfrequent toepassingen	P. Hageman
11:00	Toepassing van ELO voor III-V zonnecellen	J. Schermer
11:30	InP kristalgroei voor telecommunicatie lasers	A. van Geelen
12:00	Kristalgroei van GaInAsN voor vertical cavity lasers	M. Leys
12:30	LUNCH	
13.30	ALGEMENE LEDENVERGADERING	NVKG
	Programma rondleiding	
14:30	Inleiding rondleiding	A. van Geelen
15:00	Rondleiding Uniphase	
16:15	BORREL EN AFSLUITING	

Scanning Probe Dag 2000

This year the 'Nederlandse Scanning Probe dag' will be held on friday, 3 November 2000 in the Aula Congrescentrum at the TU Delft. The aim of the meeting is to gather scientists working on Scanning Probe Microscopy in Physics, Chemistry and Biology. The program will include 2 invited talks, 8 oral presentations anda poster session.

Informatie: http://vortex.tn.tudelft.nl/spmdag/

International School on Crystal Growth of Materials for Energy Production and Energy-saving Applications

The International School on Growth of Materials for Energy Production and Energy-Saving Applications, promoted by the IUCr Commission on Crystal Growth and Characterisation of Materials, will be held during March 5-10, 2001 at the Adbus Salam Center for Theoretical Physics, Trieste (Italy). The School will be chaired by R. Fornari (CNR-MASPEC Inst., Italy) and will include a number of lectures on: general crystal growth principles, crystal growth techniques, growth and characterisation of semiconductors for solar cell fabrication, superconductors for energy storage, wide bandgap semiconductors for white light production, small bandgap semiconductors for thermoelectric applications, soft magnetic materials and more. Lectures will be given by a panel of international experts.

Contact: Prof Lucia Sorba <sorba@sci.area.trieste.it> Secretary
Web site: http://www.semiconductors.co.uk/cgm-epes.htm

Recente proefschriften

Joop ter Horst

Titel proefschrift	Molecular Modelling and Crystallization Morphology, Solvent Effect and Adsorption
Gepromoveerd	23 mei 2000, Technische Universiteit Delft
Promotor	Prof.Dr.Ir. G.M. van Rosmalen

Crystallization is a separation and purification process, which in industry generally involves large volumes. The process of crystal growth takes place at the crystal surface where building units (generally crystal compound molecules) are incorporated at steps on the surface. This implies that although industrial crystallization involves large volumes, the incorporation of crystal building units is still a molecular level process. The energies of the system on a molecular level determine the growth related crystal properties such as the crystal shape. Molecular modelling is a tool to investigate these molecular scale processes and molecular level energies. This research demonstrates to what extend molecular modelling can be used to explain industrial crystallization behaviour.

Foreign compounds like additives and solvents can have a large effect on the crystal quality (morphology, inclusion content) and the process handling (filterability, scaling). These are related to the effect on the growth rates of the different crystal surfaces, and thus to the interaction of the foreign compounds with the different crystal surfaces. A procedure leading to a tool to predict the effect of a foreign compound is presented in chapter 2, and is followed throughout this thesis.

Following this procedure first all possible surface structures have to be determined. This was done for the crystal compound RDX with aid of a periodic bond chain analysis in chapter 3. From that it was determined which surface structures might be experimentally present when RDX is crystallized from a solution.

The crystal compound RDX can be used as an explosive compound. The product quality of an explosive compound like RDX largely depends on the crystal quality. For instance the crystal morphology is related to the packing density (explosive power) of the product and the internal quality of the crystal product determines the sensitivity of the explosive product. To increase the knowledge on RDX crystallization small scale in situ cooling crystallization experiments in stagnant media were performed where the crystal growth was followed with aid of a microscope (chapter 4). The solvent was found to have a tremendous effect on the RDX crystal morphology. Furthermore a minor impurity in the RDX/cyclohexanone crystallization system affecting the crystal growth process was identified. This impurity is likely to originate from a reaction between the solvent cyclohexanone and a synthesis byproduct, incorporated in the crystals and released upon dissolution. Thus habit modifying impurities not only originate from solvent or crystal compound but can also be formed upon dissolving the crystal compound in a solvent. Large packing densities of an RDX product can be obtained by using bi- or trimodal mixtures of different crystal size distributions. Continuous antisolvent crystallization was tested as a crystallization method for making small crystals to use in such mixtures. In the case of RDX antisolvent crystallization water was used as antisolvent while -butyrolactone or acetone was used as a solvent. Very large single crystals were however obtained while also agglomeration of the crystals occurred. These results show that RDX antisolvent crystallization is not the most suited method to produce small RDX crystals (chapter 5).

A common problem in industry is scaling, the unwanted crystallization on walls and in pipes. This can be prevented by introducing

an effective additive in the system. The large interaction between additive and crystal surface retards the growth of the crystals. Both the experimental adsorption isotherms and the adsorption energy calculated with aid of molecular modelling were determined for a number of polyelectrolytes onto calcium fluoride as a function of the pH (chapter 6). The calculated adsorption energy of a polyelectrolyte and the experimental surface concentration plateau value for a polyelectrolyte show the same trend as a function of pH. For the prediction it is of great importance that the morphologically important surface structures are known since these are as important for a valid prediction as the adsorbing compound.

Up to now there was not much attention in literature for the reason behind the large effect of a solvent on the crystal morphology. Molecular modelling is a good tool to search for an explanation for the solvent effect. RDX was taken as the model compound. The interaction energy of solvent and crystal surface was estimated by calculating the energy of one solvent molecule on all these surface structures (chapter 7). The calculated adsorption energies of a solvent molecule on all crystal surface structures were used to adjust the order of importance of the crystal surfaces in that solvent. Although there are some discrepancies between the experimental and calculated order of importance this seems to be a quick and simple solvent screening method. Modelling systems with more solvent molecules representing the boundary layer give a more accurate energy description of the system.

The potential energy change in the solvent upon presenting it to a certain crystal surface was calculated (chapter 8). This surface induced potential energy change can be used as a solvent effect correction factor for the vacuum attachment energy of a crystal surface structure. The surface induced potential energy changes calculated for the solvent -butyrolactone onto both the (200) and the (210) crystal surfaces of RDX give an explanation why the (210) crystal surface becomes morphologically very important while the (200) crystal surface does not develop when RDX is crystallized from -butyrolactone.

The permeability of a zeolite membrane for small molecule gases was estimated using molecular modelling (chapter 9). As model compounds the all-silica zeolite DD3R and alkane and alkene gases were chosen. The DD3R crystal structure contains a two-dimensional pore structure consisting of relatively large cages interconnected with relatively narrow passage. The permeability is determined by the diffusion of the gas through the membrane and the solubility of the gas in the membrane. The diffusion coefficient is determined by the activation energy needed for a gas molecule to jump through the passage to an adjacent cage while the concentration is determined by the adsorption energy of the adsorbent in the cage. Both the activation and adsorption energy were calculated with aid of a specially developed molecular modelling method for a number of small alkane and alkene gases. High selectivities for the compounds trans-1,3-butadiene and propene were found.

Edzer Huitema

Titel proefschrift   Crystal growth and defect generation
Gepromoveerd   23 november 1998, Universiteit Utrecht
Promotor   Prof.Dr. J.P.J.M. van der Eerden

Dit proefschrift beschrijft numerieke simulaties van kristalgroei, waarbij een continuüm model gebruikt wordt, namelijk het Lennard-Jones model. Centraal staan de structuur van de grenslaag tussen het kristal en de moederfase en het ontstaan van defecten tijdens kristalgroei op micro-scopische lengte- en tijdschalen. Tot nu toe zijn voornamelijk rooster modellen gebruikt voor de studie van kristalgroei op atomaire schaal. Deze zijn zeer belangrijk gebleken voor het onderzoek naar de relatie tussen oppervlakte verruwing en de kristalgroei snelheid en de invloed van schroefdislocaties en andere lijndefecten op de kristalgroei kinetiek. Rooster modellen kunnen gebruikt worden voor de beschrijving van het kristalgroei proces op een wat grotere lengte- en tijdschaal dan mogelijk met het Lennard-Jones model, waar de lengte schaal in de orde van 10 nm (10^4 deeltjes) en de tijdschaal in de orde van 1 ns ligt. Dit komt doordat het Lennard-Jones model, terwijl het toch een van de eenvoudigste continuüm modellen is, meer rekenintensief is dan rooster modellen.

Het Lennard-Jones model geeft extra informatie in gebieden en voor processen waar de beschrijving met een rooster slecht is. Dit is vooral het geval in de grenslaag tussen het kristal en de moederfase en voor de vorming van defecten tijdens het groeiproces, waarbij deeltjes van hun rooster posities afwijken.

Hoofdstuk 2 is gewijd aan defect formatie tijdens kristalgroei. Hierin is een model geformuleerd dat defect formatie tijdens kristalgroei beschrijft en worden een aantal simulatie voorbeelden gegeven van kristalgroei en defect heling. Het centrale idee achter het model is dat tijdens het kristalgroei proces defecten aan het kristal oppervlak gevormd worden, waarvan sommigen helen terwijl anderen in het uiteindelijke kristal terechtkomen. De reductie van het vrije energie overschot van het defect wordt gezien als de drijvende kracht achter defect heling. Twee defect parameters worden gebruikt: de defect grootte (hierbij wordt een bolvormig defect verondersteld) en de defectdiepte ten opzichte van het kristal oppervlak. Een kritische diepte is gedefinieerd, die bepaalt of een defect heelt of in het kristal wordt opgenomen. Defecten minder dan de kritische diepte van het oppervlak helen, defecten rond de kritische diepte van het oppervlak krimpen aanmerkelijk en andere defecten worden ingebouwd zoals ze gevormd zijn.

In hoofdstuk 3 worden de thermodynamische eigenschappen en de locale ordening van vloeibare racemische mengsels onderzocht. De thermodynamische eigenschappen worden bepaald door metingen van de chemische potentiaal en de enthalpie van de twee componenten. De locale ordening in de vloeistof fase wordt onderzocht door middel van bindingsoriëntatie orde parameters. Deze parameters, die afgeleid zijn van de sferische harmonische functies, worden in de laatste drie hoofdstukken van dit proefschrift gebruikt om de structuur in de grenslaag tussen het kristal en de moederfase te onderzoeken. Hier worden ze gebruikt om de structuur van de locale omgeving rondom een deeltje in de vloeistof te analyseren.

Eerst worden mengsels met verschillende interactiesterkte tussen de twee enantiomeren onderzocht, met als resultaat fasescheiding bij lage interactiesterkte en een glasovergang bij hoge interactiesterkte. De metingen van de locale structuur worden gebruikt om een correlatie te vinden tussen een aantal kristalstructuren en de locale structuur in de vloeistof. In dit geval wordt geen hoge correlatie gevonden. Als tweede worden mengsels met verschillende sterische hindering onderzocht. Dit resulteert in locale

ordening van de vloeistof, wat aangegeven wordt door een duidelijke correlatie tussen de locale vloeistofstructuur en de NaCl (keukenzout) structuur en een aantal dichtstgepakte strukturen.

In hoofdstuk 4 wordt een semi-quantitatieve vergelijking gemaakt tussen dynamische processen gesimuleerd met de Moleculaire Dynamica (MD) methode en de Monte Carlo (MC) methode. Dit zijn de twee methoden die gebruikt worden voor het simuleren van het Lennard-Jones model. De MD methode is deterministisch en in staat om de transporteigenschappen van klassieke veel-deeltjes systemen uit te rekenen. Dit is niet duidelijk voor de MC methode, omdat dit een stochastische methode is die gebruik maakt van random getallen om een volgende configuratie te genereren. Wanneer de correlatie tussen de configuraties in MC geïnterpreteerd wordt als evolutie in the tijd, is het mogelijk om een tijdschaal voor MC simulaties te definiëren. Het voordeel van MC, zelfs als de dynamica van het systeem belangrijk is, is dat het flexibeler is dan MD wanneer numeriek gecompliceerde systemen, zoals kristalgroei uit oplossing gesimuleerd worden. Er kunnen onfysische processen gebruikt worden in MC die de te simuleren fysische tijden in de simulatie kunnen vergroten. De betrouwbaarheid van de MC tijdschaal is onderzocht door snelheids auto-correlatie functies te meten van Lennard-Jones vloeistoffen met MC zowel als MD. We laten zien dat de dynamica gegenereerd met MC vergelijkbaar is met die van MD op tijdschalen groter dan 1 ps. De MC tijdschaal, gedefinieerd door middel van zelf-diffusie coëfficiënten in de vloeistoffase, is getest met kristalgroei simulaties uit de smelt, uitgevoerd in MC en MD. De gemeten groeisnelheden zijn vergelijkbaar.

In hoofdstuk 5 worden MC simulaties van kristalgroei uit de smelt uitgevoerd, gebruik makend van de tijdschaal gedefinieerd in hoofdstuk 4. Dit is het eerste van drie hoofdstukken waarin de structuur van de grenslaag tussen het kristal en de moederfase onderzocht is. Groei van de (100), (111) en (110) oppervlakken van het Lennard-Jones kristal is gesimuleerd, waarbij een lineaire afhankelijkheid tussen de groeisnelheid en het chemische potentiaal verschil tussen het kristal en de smelt gevonden is. De kinetische coëfficiënten zijn bepaald, waarbij gevonden is dat die van het (100) vlak twee keer zo hoog is als op grond van traditionele kristalgroei theorie verwacht werd (de BFDH wet).

Gedetailleerde metingen van de structuur van de grenslaag tijdens groei zijn uitgevoerd met gebruik van bindingsorientatie orde parameters. Een nieuwe orde parameter is gedefinieerd die kristallijne deeltjes onder-scheidt van vloeistofachtige deeltjes op grond van locale symmetrie eigenschappen. De metingen geven aan dat er een sterke gelaagdheid van de smelt aanwezig is voor het (bewegende) grensvlak voor alle drie kristalvlakken. De vloeistoflagen van de (111) and (110) oppervlakken hebben ongeveer dezelfde interlaagafstand als die van de corresponderende kristalvlakken. Het (100) oppervlak daarentegen heeft vloeistoflagen beginnend met de (100) kristalvlak afstand en eindigend met de (111) kristalvlakafstand. De conclusie is dat deze speciale kristal-smelt interactie ervoor zorgt dat de kinetische coëfficiënt voor het (100) vlak twee keer zo hoog is als verwacht.

In hoofdstuk 6 worden MC simulaties van kristalgroei uit een Lennard-Jones oplossing uitgevoerd. De tijdschaal gedefinieerd in hoofdstuk 4 en de orde parameter zoals gedefinieerd in hoofdstuk 5 worden gebruikt. Een onfysisch proces wordt ingevoerd dat de molfractie opgeloste stof in de oplossing constant houdt en dat de mengsnelheid verhoogt. Dit resulteert in simulaties waarbij veel langere tijdschalen gesimuleerd kunnen worden. Voor het eerst wordt in simulaties van het Lennard-Jones model het twee-dimensionale nucleatie groeimechanisme waargenomen, wat blijkt uit een niet-lineair verband tussen de groeisnelheid en het chemische potentiaal verschil. Een overgang van een niet-lineaire naar een lineaire groeiwet is waargenomen wanneer de

interactie tussen de opgeloste stof en het oplosmiddel verhoogd wordt. Een vergelijking tussen de resultaten behaald met het Kossel model (een rooster model) en onze resultaten is gemaakt door middel van de α-factor, gedefinieerd door Jackson. In het Kossel model is de verruwingsovergang gevonden bij $\alpha_R \approx 2.9$, terwijl wij $\alpha_R \approx 2.5$ en $\alpha_R \approx 3.1$ vinden voor twee series van groei experimenten. Dit toont aan dat er een kwalitatieve overeenstemming is tussen het Kossel en het Lennard-Jones model wat betreft de verruwingsovergang.

De structuur van de grenslaag is onderzocht door middel van de orde parameter, wat laat zien dat er een sterke ordening van de oplossing voor het grensvlak optreedt, vooral tijdens ruwe groei. Dit toont aan dat de totale groeisnelheid voor ruwe groei sterk beïnvloed zal worden door de kinetiek in de eerste (twee tot drie) lagen voor het grensvlak. Een aantal simulaties, waarbij een ander onfysisch proces gebruikt wordt, bevestigt dat die geordende lagen bestaan en dat ze inderdaad belangrijk zijn voor de totale kinetiek.

In hoofdstuk 7 worden simulaties van kristalgroei uit een verontreinigde smelt uitgevoerd. De verontreinigingen zijn een tweede Lennard-Jones deeltje, tot 20% aanwezig in de smelt. Thermodynamische metingen zijn uitgevoerd met verschillende verontreinigingen om een voor onze simulaties geschikte verontreiniging te vinden. De metingen zijn ook belangrijk om

de evenwichts-segregatiecoëfficiënt te vinden (dit is de molfractie verontreiniging in het kristal gedeeld door de molfractie in de smelt). Een aantal verschillende MC simulatietechnieken worden gebruikt, geïntroduceerd in hoofdstuk 6, waarmee segregatiecoëfficiënten gemeten worden aan een groeiend kristaloppervlak. Drie gevallen worden onderscheiden: een mengsnelheid die veel hoger is dan de groeisnelheid, een lagere maar nog steeds verhoogde mengsnelheid en de normale (niet verhoogde) mengsnelheid. In het geval van zeer hoge mengsnelheid, is de molfractie verontreiniging dicht bij de evenwichts-waarde. In het geval van verhoogde mengsnelheid is de molfractie verontreiniging in het kristal boven de evenwichtswaarde en is de groeisnelheid lager dan die gemeten met zeer hoge mengsnelheid. Wanneer de normale mengsnelheid gebruikt wordt, is de groeisnelheid nul, wat verwacht is op grond van de thermodynamische metingen

De metingen van de structuur van de grenslaag tijdens de simulaties met verhoogde mengsnelheid tonen aan dat er een gradiënt in samenstelling in de smelt opgebouwd wordt, wat een verhoogde concentratie verontreiniging voor het grensvlak geeft ten opzichte van de concentratie in de bulk van de smelt. Bij zeer hoge mengsnelheid wordt deze gradiënt niet waargenomen, terwijl bij normale meng-snelheid een klein kristallijn gebied groeit dat in evenwicht is met de smelt.

Frank Wubbolts

Titel proefschrift	Supercritical Crystallisation. Volatile Components as Anti-Solvents
Gepromoveerd	2000, Technische Universiteit Delft
Promotor	Prof.Dr. G.M. van Rosmalen

Volatile components, in particular carbon dioxide, are a promising alternative for many organic solvents in a crystallisation process. It is a non-toxic, inexpensive compound and its high volatility compared to common solvents opens opportunities for the development of innovative processes.

The solubility of many solids in carbon dioxide is very low and it is therefore less suitable as a solvent. Instead, it can be used as an anti-solvent to crystallise a solute from a solution. For the evaluation and design of the different crystallisation processes solubility data is required of solids in mixtures

of a solvent and carbon dioxide. While the relevant vapour-liquid equilibrium data are available, the solubility of solids in a mixture of a common solvent and CO_2 is not.

A new method and equipment are presented to measure the solubility of solids in mixtures of CO_2 and a solvent at a constant temperature and pressure. The systems studied were p-acetamido phenol in ethanol or acetone, cholesterol in diethyl ether, acetyl salicylic acid in acetone and 4-hydroxy benzoic acid in acetone. The solubilities were measured at 295 K, 7 MPa and at 315 K, 10 MPa. A solubility model was developed that calculates the activity coefficient of the solute in the solution with the Peng-Robinson equation of state

The new method for the measurement of the solubility is a practical alternative to techniques that require an analysis of the equilibrium composition. The measured solubilities were successfully correlated with the solubility model. When it is present at a low concentration carbon dioxide is generally not very effective as an anti-solvent. Its effectiveness increases at a higher concentration.

An option to use a gas, like carbon dioxide, as an anti-solvent is to pressurise a solution with the anti-solvent vapour. As the vapour dissolves, it reduces the solubility of the solute. Dissolution of the vapour in the solution is accompanied by a considerable adiabatic temperature change, and mass transfer from the vapour to the liquid limits the dissolution rate of the anti-solvent. These factors hamper control over the carbon dioxide concentration in the solution and therefore over the supersaturation.

To prevent heat effects upon the addition of the CO_2 the solution is first pressurised with helium. Liquid or supercritical carbon dioxide is then mixed with the solution. Ideally the carbon dioxide concentration in the solution can be adjusted independent of the pressure and heat effects are much reduced. The crystallisation process was modelled with the method of moments, to study the development of the supersaturation in time.

The developed isobaric procedure for precipitation, where either liquid or supercritical carbon dioxide is mixed with the solution, can quickly increase the anti-solvent concentration in the mixture. Although part of the carbon dioxide dissolves in the helium vapour the crystallisation procedure is well controlled and yields slightly aggregated crystals of about 200 µm. The numerical model, which uses simple kinetics for nucleation growth and aggregation, can describe the crystallisation process and provides insight in the sequence of events during the crystallisation process. In the experiments as well as in the simulations, the influence of the process conditions on the size and shape of the product remains limited. This is inherent to the semi-batch mode of operation and the crystallisation kinetics.

After its use in a semi-batch process was demonstrated, where the process conditions change with time, a crystalliser was developed that operates in a continuous mode. In a continuous crystalliser the process conditions are constant and the supersaturation is relatively low compared to a batch process. This is expected to allow better control over the growth of the crystals. In addition, the nucleation and growth rates of the crystals can then be determined form the crystal size distribution by applying the MSMPR model.

The continuous crystalliser was operated at a constant pressure above the saturation pressure of carbon dioxide. Liquefied carbon dioxide was mixed with a solution in a mechanically agitated vessel, while the crystal slurry was continuously withdrawn. The crystals were recovered from the mother liquor in a separate filtration unit. Experiments were performed with the crystallisation of ascorbic acid from ethanol. The influence was examined of the process parameters on the yield and the size and shape of the particles.

All used model compounds showed strong aggregation which hampered operation by forming encrustation on the wall and internals

of the crystalliser. With ascorbic acid, an experiment of a longer duration was possible. Although the steady-state solute concentration does depend on process conditions, there was no clear influence on the size or morphology of the primary crystals or aggregates.

Instead of mixing a solution with CO_2 in a stirred vessel the solution can also be injected into a vessel filled with compressed CO_2 vapour. In such a process the phase behaviour of the CO_2 and the solvent results in several regions of operation where different mechanisms contribute to the generation of the supersaturation that drives the crystallisation process.

In a series of experiments ethanol was sprayed into carbon dioxide or helium vapour, to observe the influence of the pressure on the behaviour of the jet. In the CO_2 vapour the nozzle forms droplets below a certain pressure. With a numerical model the mass transfer was simulated between droplets of ethanol or dimethyl-ether and carbon dioxide vapour. This provides insight in the rate of change of the droplet size and the carbon dioxide concentration at a constant pressure and shows the influence of the feed ratio of CO_2 and solvent.

Depending on the pressure there are two distinctly different regions of operation. Above the mixture-critical or saturation pressure there is no interface between the solvent and the carbon dioxide vapour and the two components merge by mixing. Below that pressure the integrity of a droplet is preserved by the vapour-liquid interface. Here the conditions can be chosen such that the entire droplet is evaporated by the CO_2. This evaporation process is much faster for a solvent with a high vapour pressure, like dimethyl-ether, than for ethanol.

The phase behaviour of the solvent and carbon dioxide results in two distinctly different operating regions. Above the saturation pressure of the carbon dioxide or the critical pressure of the mixture, the solvent and carbon dioxide are miscible while below that pressure there is an interface

between the liquid and the vapour phase. In the latter case the crystallisation process can be spatially confined to a droplet, while the CO_2 can extract the solvent.

The mechanisms that contribute to the supersaturation are investigated for the crystallisation of cholesterol from diethyl-ether or from dimethyl-ether at a temperature of 323 K. The solutions were injected with a hydraulic nozzle, and the influence was determined of the process conditions on the yield and morphology of the product. Simulations were performed to estimate the rate of increase of the supersaturation inside droplets of a cholesterol solution in diethyl ether.

The shape and size of the cholesterol particles that were formed below the mixture-critical pressure clearly show that the crystallisation process was spatially confined to the droplets that were produced by the nozzle. The initial size of those droplets determines the size and shape of the produced particles. According to the simulation a very high supersaturation can be reached in those droplets within 50 ms. Above the mixture-critical pressure there is no sign of confinement and the crystallisation takes place in a continuum.

Also polymers can be precipitated by adding CO_2 to a solution. Potentially the use of a volatile anti-solvent like CO_2 reduces the residual content of volatiles in the material. For industrial applications it is important to be able to control the size and size distribution of the particles with the process conditions.

The polymer PPE (poly 2,6 dimethyl 1,4 phenylene ether) was precipitated from a concentrated solution in toluene using high-pressure carbon dioxide as an anti-solvent. The precipitate was characterised by the particle size, the particle size distribution, and the degree of crystallinity of the solid.

The product consists of aggregated PPE particles of approximately 1 μm. Whereas the size of these primary particles appears to be independent of the process conditions, the extent of aggregation can be influenced by the process conditions. The temperature has

the largest effect on the aggregation process. At a relatively high process temperature of 333 K aggregates are obtained of approximately 700 µm, with a narrow size distribution.

Compressed volatile components are a technically feasible alternative for common solvents in particle formation processes. In particular carbon dioxide is an attractive choice because it is inexpensive and non-toxic. In a crystallisation process it can be used as a solvent, anti-solvent or extractant. An important advantage of a volatile component is that the solid product is immediately obtained as a dry powder after depressurisation.

The requirements are outlined of a crystallisation process for micronisation, purification or encapsulation. With the solubility data that is available for acetaminophen in mixtures of ethanol and CO_2, and for cholesterol in diethyl ether and

CO_2 the optimum conditions are chosen for the different crystallisation processes. The specific CO_2 consumption was determined from the solubilities of the two systems and the specific cost of the operations was calculated from cost estimates of fresh and recycled CO_2. Different methods are portrayed to recover the volatile anti-solvent from the mother liquor after crystallisation.

A micronisation process that uses CO_2 as a solvent has a specific CO_2 consumption (SCC) in the order of 1500 kg per kg of product. When it is used as an anti-solvent the highest SCC, which is required for micronisation, requires about 70 kg per kg product and a yield close to 98 % can be attained. The SCC shows a minimum of about 5 kg per kg solid, but in that case the yield remains low. The specific cost of a micronisation process with CO_2 as an anti-solvent is estimated to be about 100 times less than with CO_2 as a solvent.

Tjakko Zijlema

Titel proefschrift	The antisolvent crystallisation of sodium chloride
Gepromoveerd	1999, Technische Universiteit Delft
Promotor	Prof.Dr. G.M. van Rosmalen en Prof.dr.ir. G.J. Witkamp

The aim of this study is to develop an antisolvent crystallisation process, constituting the antisolvent crystallisation and recovery steps, that provides NaCl crystals with a quality equivalent to the quality of the salt crystals produced by evaporative crystallisation at a reduced energy consumption.

The main criteria for the selection of the antisolvent are the extent to which its presence reduces the sodium chloride solubility in water, and its separability from the aqueous phase after crystallisation. With respect to this diisopropylamine, dimethylisopropylamine and 2-isopro-poxyethanol are suitable antisolvents for the crystallisation of NaCl. These antisolvents are partially miscible with a brine showing Lower Critical Solution Temperatures close to room temperature. The salt can be

crystallised at temperatures below the LCST in the single liquid phase area, and the antisolvent can be recovered at elevated temperatures in the double liquid phase area, where the mutual solubilities of the antisolvents and water are low.

Important to the energy household is the enthalpy of mixing of the antisolvent and water. The highest measured enthalpies of mixing for the amine-water systems were -105 $J/g_{mixture}$ for dimethyl-isopropylamine-H_2O and -81 $J/g_{mixture}$ for diisopropylamine-H_2O at amine concen-trations of 49 wt% and 60 wt% respectively.

An experimental setup has been built for the investigation of the continuous antisolvent crystallisation. The 1 liter crystalliser can be used at temperatures of -20 to 200 °C and at pressures of up to 20 bar. To prevent corrosion Hastelloy-C has been used as the

main material of construction. Solid as well as liquid samples can be taken and the crystalliser is equipped with an in-line image probe for the visualisation of the crystals inside the vessel.

The size, shape, purity and degree of agglomeration of the particles formed by continuous antisolvent crystallisation with diisopropylamine or dimethylisopropyl-amine has been investigated. The formed sodium chloride crystals did not satisfy the product quality requirements. The product generally consisted of small and agglomerated crystals with amine uptakes of 40 to 630 ppm, which is too high. An amine uptake of less than 10 ppm is essential, since the amines form the explosive compound NCl_3 in the electrolysis of the salt.

The antisolvent uptake can be reduced significantly if first $NaCl.2H_2O$ is formed by antisolvent crystallisation, which is subsequently recrystallised into NaCl in a purer brine. The purification that can be obtained by applying this recrystallisation step has been studied in batch experiments in brines containing either 0 or 5 wt% of dimethylisopropylamine. The recrystallisations carried out at various temperatures, gave 100 to 900 fold purity increases of the solid phase. The average dimethylisopropylamine concentration in the $NaCl.2H_2O$ was ca. 1000 ppm, whereas the dimethylisopropylamine concentration in the NaCl product was between 1 and 6 ppm.

The influence of the antisolvent on the kinetics of nucleation and crystal growth and the effect of the high levels of supersaturation, often encountered in antisolvent crystallisation, on mainly particle size, shape and agglomeration has been investigated. Continuous crystallisation experiments demonstrated that NaCl crystals formed by antisolvent crystallisation in the single liquid phase area are generally small and agglomerated. This results from extensive primary nucleation at the antisolvent inlet in the crystalliser. The supersaturation at the antisolvent inlet and with that the primary nucleation rate can be reduced by adding water to the antisolvent, resulting in the formation of larger less agglomerated crystals. This however, reduces the yield. An alternative is to crystallise the salt from the two liquid phase area. Due to the limited miscibility of the antisolvent and the crystalliser contents in the double liquid phase area, the supersaturation at the antisolvent inlet is lower, resulting in the formation of large single crystals. However, the yield in the double is lower than in the single liquid phase area.

To get a better understanding of how the size distribution of the formed particles is influenced by locally high supersaturations a tool has been developed. It enables the measurement of primary nucleation rates and induction times as a function of the antisolvent concentration at supersaturation levels that prevail in the area of the crystalliser antisolvent inlet. To exclude the influence of mixing on the measured kinetic data, the brine and the antisolvent are mixed rapidly in an opposite tee mixer. The mixed flows that leave the tee mixer are fed to an optical flow cell. In this cell the particle concentrations in the antisolvent-water-salt mixture can be determined with an optical particle counter at various distances, or reaction times, from the point where the antisolvent and the salt solution are mixed.

The reproducibility of the nucleation rate measurements carried out in this experimental setup was generally poor. This can be attributed to scaling. The three most successful nucleation rate measurements, carried out at antisolvent concentrations of 40, 50 and 60 wt% and supersaturation ratios of 1.12, 1.20 and 1.32, have been analysed. Despite of the differences in antisolvent concentration and supersaturation the measured nucleation rates were almost identical and were in the order of 10^8 (m^{-3} s^{-1}). The calculated induction times varied between 0.33 to 0.58 s and decreased at an increasing antisolvent concentration.

Guidelines have been provided for the selection of the optimal process conditions and the antisolvent for the antisolvent

crystallisation of inorganic salts, that are produced by evaporative crystallisation. Based on these guidelines processes have been designed for the production of NaCl, either via the antisolvent crystallisation of NaCl or via the antisolvent crystallisation of $NaCl.2H_2O$ followed by a recrystallisation step. The estimated costs and energy consumptions of these antisolvent crystallisation processes and of the traditional four effect evaporative crystallisation route have been compared. The calculations demonstrated that the reduction in energy costs can be as much as 29 %, if NaCl is crystallised directly by antisolvent crystallisation. The estimated fixed capital costs however, are 4 to 50 % higher for the direct antisolvent crystallisation of NaCl. At an energy price exceeding 3.3 times the current energy price level, the direct antisolvent crystallisation of NaCl becomes economically more attractive than the evaporative crystallisation process. In the two step process, including the recrystallisation of $NaCl.2H_2O$, large and pure NaCl crystals can be produced at the expense of increased operating costs.

Harald Oosterhof

Titel proefschrift	Antisolvent crystallisation of sodium carbonate
Gepromoveerd	1999, Technische Universiteit Delft
Promotor	Prof.dr.ir. G.J. Witkamp en Prof.Dr. G.M. van Rosmalen

Crystallisation is, directly after distillation, the most often applied separation technique in chemical industry. Crystallisation is very selective and consumes mostly less energy than other separation processes. Its driving forces can be created by either removing the solvent or by decreasing the solubility of the dissolved compound.

In this work, fundamental and practical aspects of antisolvent crystallisation were investigated aiming to produce a better quality crystal product (for instance crystal size distribution, purity and bulk density) at lower energy costs.

The principle of antisolvent crystallisation, reducing the solubility by binding the primary solvent to a so-called 'antisolvent', is often encountered in pharmaceutical crystallisation, but hardly ever in industrial bulk crystallisation. An ideal antisolvent crystallisation process contains three main sections. In the first section, the dissolved salt is mixed with an antisolvent. Due to the antisolvents ability to bind water, the solubility of the salt is reduced, resulting in the formation of a solid phase. Subsequently, in the filtration section, the liquid phase is separated from the crystals, leaving a clear filtrate that is sent to the antisolvent regeneration section where solvent and antisolvent are separated. Finally, the antisolvent is recycled to the crystallisation section while the water can used elsewhere at the production location, for instance for the dissolution of raw material.

The introduction of an organic antisolvent will always give rise to a lot of initial uncertainties. It will have a large influence on the behaviour of crystallising mixture: physical properties like density and viscosity will change, the solubility of the solute decreases and the kinetics of the process will drastically be altered, both nucleation, growth and agglomeration kinetics are strongly influenced by the composition of and supersaturation in the crystallising mixture. Also, the antisolvent might interact with the crystal product, acting as a habit modifyer, changing the shape and size of the crystals.

The work presented in this thesis explores characteristics and opportunities of antisolvent crystallisation. Two model salts are used, sodium nitrate and sodium carbonate. Both salts are produced in large quantities while their energy requirements are high due to the costs of the evaporation

of water. They also have their specific operational problems.

In order to study the growth of sodium nitrate (Chapter 2), a microscopic setup was built in which crystals were nucleated and grown from different mixtures of water and antisolvent isopropoxyethanol. The growth rate was found to be linearly dependent on the applied concentration difference. The mass transfer coefficient was predicted accurately using only density, viscosity and solubility input data.

A closer look at the solid-liquid interface (Chapter 3) was carried out using molecular dynamics. The molecular modeling packages Cerius^2 and Insight/Discover were used for the simulations and the COMPASS98.01 force field was applied. The results of a 20 nanoseconds NVT (constant number of molecules, volume and temperature) run yielded information about the configuration of both solvents at the {012} $NaNO_3$ surface. It was found that the sodium nitrate surface is preferentially covered with water molecules that are highly ordered. On top of this layer, a layer of isopropoxyethanol is distinguished. From the observations that the antisolvent isopropoxyethanol is not present at the crystal surface, it was concluded that the experimentally determined growth rate was indeed the result of changed bulk characteristics and not because of the interaction of isopropoxyethanol with the crystal surface.

The second part of this thesis describes the invention, development and design of improved processes for the production, and in particular the densification, of soda ash. At present, soda ash is produced either by the Solvay process or by the monohydrate process. If the mineral trona ($Na_2CO_3.NaHCO_3.2H_2O$) is available, monohydrate is crystallised that is heated in a second calciner producing anhydrous dense soda. With the Solvay process, sodium bicarbonate is crystallised. During calcining, this intermediate is transformed into anhydrous soda ash, with a bulk density of about 550 kg/m^3. A final densification step

can be applied to increase (at high energy costs) the bulk density to little over 1000 kg/m^3. Both processes produce a brittle product with a low bulk density. There is a need for soda with a better quality: a crystalline product with a high bulk density a low chloride concentration. Additionally, the energy costs need to be decreased.

A first attempt to produce super dense soda ash was carried out using 1-butanol as antisolvent (Chapter 4). Continuous antisolvent crystallisation experiments were carried out at 160 to 200°C. The crystal product however contained small particles: the volume averaged diameter of the agglomerated crystals was between 60 and 100 μm. The product contained 2 w% antisolvent on the average. Both the particle size and the impurity of the product are caused by the high supersaturations during crystallisation.

A better quality soda ash can be produced by evaporion or recrystallisation in the presence of high-boiling antisolvents. Antisolvents in general have the tendency to decrease the water activity of a mixture. The required anhydrous phase is stable at temperatures above 109°C. This so-called transition temperature is located above the boiling temperature of a saturated sodium carbonate solution which means that atmospheric evaporative crystallisation will always produce sodium carbonate monohydrate, the phase that is stable between 32 and 109°C. The addition of a high-boiling antisolvent has three important effects on the crystallising mixture: the solubility of the solute is decreased, the boiling point of the mixture is increased and the transition temperature is decreased due to the decreased water activity.

Several high-boiling antisolvents were tested for their phase behaviour and their ability to decrease the solubility of soda (Chapter 5). Two antisolvents were promising enough to subject them to a closer examination.

The antisolvents ethylene glycol and diethyleneglycol were used in a series of crystallisation experiments where pure

antisolvent and a soda solution were added simultaneously to the reactor (Chapter 6). With both antisolvents it was possible to produce anhydrous soda at atmospheric conditions when the temperature and the weight fraction antisolvent in the mixture where sufficiently high. The bulk density is equal to that obtained in current processes when these apply a densification step: about 1000 kg/m^3.

An attempt was made to predict the influence of type and amount of antisolvent on the transition temperature of soda (Chapter 6). Two models were developed that connected the water activity of the solution to the temperature at which anhydrous and monohydrous sodium carbonate are in equilibrium. Both models were found to be very accurated after validation by continuous experiments.

Finally, ethyleneglycol was used to produce super dense soda ash using two new processes: one by means of evaporative crystallisation from a mixed solvent (Chapter 7) and one by a double recrystallisation, also in a mixed solvent (Chapter 8). Evaporative crystallisation from a mixed solvent is carried out similarly as evaporative crystallisation in the monohydrate process. A certain amount of glycol, is added to the feed stream to the crystallisation section in which the water is evaporated. Sufficient glycol is added to ascertain the stability of the anhydrous form at the boiling conditions in the crystalliser. Similarly as in the monohydrate process, water still has to be evaporated which means that no energy is saved. However, this patented process directly produces super dense soda ash with bulk densities of over 1500 kg/m^3. An economic evaluation showed that the conversion of a conventional monohydrate plant with a annual capacity of 500 kton into a 'mixed solvent' plant would

cost approximately 2.5 M . Using the decrease in annual total costs of approximately 2.7 M , a payback time of less than one year was calculated.

The principle of evaporation from mixed solvents is not an economically interesting alternative for the Solvay process. Therefor, another process is proposed to replace the so-called monohydration process during which the light soda ash is converted into dense soda ash in a calciner. The new (patent application filed) process uses the ability of the antisolvents to decrease the water activity in the crystallising mixture. Mixtures of water and ethyleneglycol were prepared in which anhydrous soda was stable closely below the boiling temperature of the solution. By adding light soda ash to this mixture at a temperature below the transition temperature, the solvent-mediated recrystallisation of light soda into monohydrous soda was induced. Subsequently heating of the suspension to slightly above the transition temperature causes the now unstable monohydrate phase, to recrystallise into anhydrate. Since during these recrystallisations the soda is completely dissolved and crystallised again twice under well controlled conditions, a pure and super dense product is crystallised with a high bulk density of up to 1350 kg/m^3. An economical evaluation of this process showed that energy costs could be decreased with almost 60% while the investments for this new plant are 27% lower than for a conventional monohydration densification plant. Conversion of a conventional plant into the newly proposed plant requires an investment of about 2 M$ which gives a payback time of less than one year with total savings of 3 M$ per year when the cost reduction in overseas transport is included.