INFLUENCE OF THE DEGREE OF IRREVERSIBILITY OF THERMAL AND MECHANICAL TREATMENT REGIME ON THE FINAL QUALITIES OF A REACTING-SYSTEM

by

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The final qualities of interest (such as grain size, chemical purity, degree of stability, transition order) of new compounds,synthesised in solid state transformation processes (chemical reactions, phase transitions) can be controlled through the evaluation of the entropy generation in the system. Thermally activated chemical reaction ($LiCoPO_4$ synthesis) and mechanically activated phase transition ($PdSe_2$ transformation) are discussed as examples. The $LiCoPO_4$ qualities of interest are grain size (less that 0.5 μm) and chemical purity (up to 98%). The pyrite structured $PdSe_2$ qualities of interest are: transition-order and degree of stability. The requirements are first-order transition and as higher as possible degree of stability. The grain size of $LiCoPO_4$ and degree of stability of $PdSe_2$ have been described by the calculation of the entropy generation in the treatment process; the chemical purity of $LiCoPO_4$ – by the reaction co-ordinate and the transition order of $PdSe_2$ – by the behaviour of the thermodynamic potential – first partial derivative in the transition point. To compute the thermodynamic functions under request, the behaviour of the treated system has been investigated by measuring the driving force of its conversion process. In the case of thermal treatment ($LiCoPO_4$) the absorbed heat flux has been measured, whereas for the case of mechanical treatment ($PdSe_2$) the applied pressure and its corresponding material's specific volume have been measured. Experiments and calculations have been carried out for $LiCoPO_4$ to establish empirical equations, giving the relationship between the heating regime parameters and final product grain size. For $PdSe_2$, the relationships between the compression regime parameters and thermodynamic potential and the degree of stability have been received by numerical calculations.

Key words: *thermal and mechanical treatment, entropy generation in chemical and physical conversions*

Introduction

Nowadays, a lot of materials, such as cathode powder, building materials and others are prepared artificially. Some applications require determined qualities of the material like grain size, degree of stability or chemical purity. In this respect, the ability to control the quality of the final product, obtained as a result of thermal or mechanical treatment is very important. The quality of any product depends on the treatment regime which can be defined by its degree of irreversibility. Hence, the quantity of entropy generated in any treatment process can be used as an instrument to control the final quality of the material under consideration. In this paper, we try to develop an approach to control some qualities of materials, obtained by thermal/mechanical treatment for the cases of thermal (heating and/or cooling) and mechanical (compression and/or expansion) treatments of solid-state transformations (chemical reactions and phase transitions) of crystallised phases. For this goal, the qualities of interest are connected to the entropy generation in the treatment-process. We hereby apply our approach to the synthesis of $LiCoPO_4$ and to the pyrite-structured $PdSe_2$.

The $LiCoPO_4$ is a crystal powder material, obtained in solid-state chemical reaction by heating the precursor mixture in electrical furnace from ambient temperature to 750 ºC. Its application is as a cathode material in Lithium-ion batteries. Good battery quality requires the cathode material powder to have chemical purity more than 98% and grain size concerning the single particles less than 0.5 μm and less than 15 μm concerning the particle agglomerates. For that reason, the $LiCoPO_4$ final qualities as chemical purity and grain size in the range ξ_{fin} 0.98 d_s 0.5 μm are interested in. The goal is to find the thermal treatment, which gives a final product with these qualities.

The $PdSe_2$ is a crystal powder material with two possible arrangements of the crystal cell depending on the pressure. Under atmosphere pressure it has PdS_2-type crystal cell. When the pressure increase (at isothermal conditions) to GPa it transits to pyrite-type crystal cell. The synthesis challenge is to keep the new obtained structure (pyrite-type) under atmospheric pressure. The final-product (new-phase) qualities under considerations are degree-of-stability and transition order. The goal is to use the new approach to determine the transition order and the transition pressure and to analyse the influence of treatment-conditions on the degree of stability of the final product.

Theoretical approach

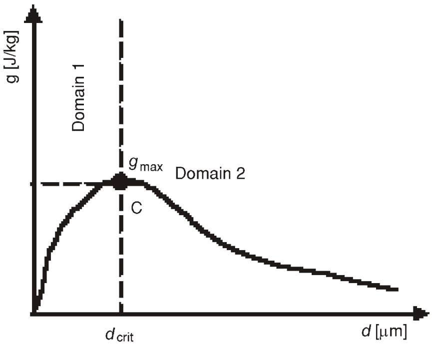

Figure 1. Thermodynamic self-stability of new phase according to its particle size

From thermodynamic viewpoint a new-phase particle could belong to two disparate domains according to its self-stability [1], fig. 1: domain of self-instability (domain 1) and domain of self-stability (domain 2). In domain 1, the increase of the particle-size causes an increase of its thermodynamic potential and, respectively, a decrease of its thermodynamic stability. On the contrary, in domain 2 an increase of the particle-size causes a decrease of its thermodynamic potential and hence, an increase of its thermodynamic stability. The boundary, separating these two domains is known as critical point.

There the new phase has maximal thermodynamic potential and maximal instability. The particle diameter at the critical point is known as critical diameter d_{crit}. If the size of a new-originated particle is bigger or equal to the critical one, this particle forms nuclei of the new phase. In case of the new-originated particle is smaller than the critical one, it is self-destroyed because of its thermodynamic self-instability. This means that its clusters are attached to extant centres (nuclei) of the new-phase.

From thermodynamic viewpoint the new phase formation in thermally/mechanically activated solid-state conversion consists of four main processes: transformation (process 1), origination of new phase nuclei (process 2), growth of single crystals (process 3), and fusion of single crystals (process 4). During process 1 (origination of new phase clusters) the initial phase (precursors) transforms chemically/physically, due to the applied thermal/mechanical impact. As a result of chemical/physical transformations, clusters of the new phase are originated. Clusters, named forms, are consisted of simultaneously formed molecules of the new phase. During process 2 (origination of new phase nuclei) the new formed clusters agglomerate themselves, striving to have higher thermodynamic stability. These agglomerates, which overcome the critical diameter, originate nuclei. The others (with diameters smaller than the critical one) are destroyed and their clusters are attached to extant stable nuclei of the new phase. It is obvious that the origination of nuclei requires simultaneous formation of large quantity of new phase clusters, respectively large number of reformed compound. This circumstance is observed only at the beginning of the conversion process. Consequently, nuclei are originated only then. When the conversion process is advanced and the quantity of simultaneously reformed compound is decreased, each new formed cluster is attached to extant single clusters, and process 2 is skipped. During process 3 (single crystal growth) the single-crystals of the new phase grow up by attaching new formed clusters. The single crystals growth goes on uniformly in all directions if available for attaching clusters exist. The growth of a single crystal is blocked in any direction, if it is reached the surface of another single crystal. Because of this, single crystals fusion is started. During process 4 (single crystal fusion) single crystals, met together, fuse each other creating physical bonds. This process is caused by the new crystals striving to decrease their specific surface, or in other words, to have higher thermodynamic stability [1].

Processes 1 and 2 develop very fast since favourable conversion conditions are ensured (for example, the critical temperature/pressure is reached). Process 3 is much slower than processes 1 and 2, as its duration depends on the quantity of originated nuclei: the more originated nuclei the shorter the single-crystal growth process, since two single crystals are met together faster. Process 4 is the slowest one. Usually, the processes 1 and 2 occur almost instantly, the process 3 takes several seconds or minutes and the process 4 – hours, days or months. It takes even years in the nature.

The quality of entire conversion process depends on the degree of irreversibility (the amount of entropy generated) of the treatment process. At the same time, the quality of the treatment process defines the qualities of the final product. Hence, if we can control the entropy generation of the treatment process, we can control the final product qualities.

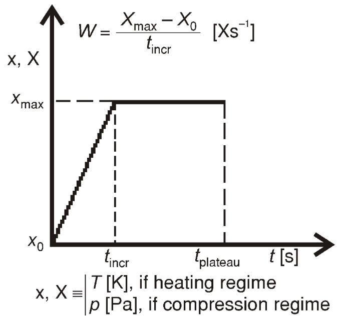

Figure 2. The type of heating /compression/ regimes

Since the new phase is formed during the heating/compression, the efforts are focussed on the heating/compression part of the treatment regime, since it is supposed that its influence is more important than this one of the cooling/expansion part. The investigated heating/compression regime consists of a temperature (pressure) increase and a temperature (pressure) plateau, fig. 2. Three main parameters determine the regime: maximal temperature, $T_{\max}$ (pressure, $p_{\max}$), heating (compression) rate w, and plateau duration t_{plat}. The maximal temperature (pressure) is fixed from the transformation nature and cannot be varied. The treatment regime parameters are the heating (compression) rate and the plateau duration, which define the degree of irreversibility. The goal is to investigate the influence of the entropy generation in treatment process on the qualities of interest of the final product.

To synthesise homogeneous new phase (zero quality variance in the entire volume) it is necessary the driving force (heating flux in case of thermal treatment and pressure in case of mechanical treatment) to be distributed uniformly in the entire treated volume. For the case of thermal treatment, the homogeneous treatment has been ensured by preliminary optimising the shape and dimensions of the treated sample. For the case of mechanical treatment, the homogeneous treatment has been ensured by default, because of the treatment device specifics. When the driving force is ensured homogeneously distributed in the treated body, the treatment process is internally reversible, since the thermodynamic parameters are uniform in the entire volume. At the same time, the difference of the values of parameters between the treated body and the heat source defines the treatment process as externally irreversible. Hence, the entropy is generated at the interface between the treated body and the environment [1] as in the case of thermal treatment and can be computed by the heat flux, transferred from the heat source to the reacting system, whereas in the case of mechanical treatment – by the applied pressure.

Experimental program

The case of thermal treatment

The thermal treatment has been realised in electrical furnace, where the heat flux is transferred by free convection and radiation. The heat transfer was evaluated complexly for the most unfavourable conditions (the highest heating rate) by adjusting the radiation heat transfer to equivalent convection heat transfer:

$$\alpha_{\text{tot}}^{w\ \max} \qquad \alpha_{\text{conv}}^{w\ \max} \qquad \alpha_{\text{rad}}^{\text{adj}\,w\ \max} \tag{1}$$

The total adjusted convection heat transfer coefficient has been estimated as α_{tot} = 155 W/m^{2}K. Then, the critical thickness to ensure a homogeneous temperature field can be computed:

$$\delta_{\mathrm{crit}} \quad \frac{\mathrm{Bi}_{\mathrm{crit}}\lambda}{\alpha_{\mathrm{tot}}} \tag{2}$$

The heat conductivity of the final product has been measured at ambient conditions by unique thermal conductivity measurement system, based on the guarded hot plate method. All measurements were done in steady-state conditions. The value of the heat conductivity was evaluated as $\lambda_{\mathrm{T}}^{\mathrm{fin}}{}_{25^{\circ}\mathrm{C}} \quad 0.65$ W/mK, and the critical thickness (δ_{crit} = = 0.5 mm), eq. (2), guarantees uniform temperature distribution at any heating rate.

The case of mechanical treatment

The compression regime was realised in diamond anvil cell with a gas driven membrane for pressure generation, which is high pressure equipment at ID30 beam-line, European Synchrotron Radiation Fellowship (ESRF). The treated sample was miniature cylinder (ϕ = 40 μm and l = 20 μm) according to the equipment requirement. This ensures uniformly distributed driving force in the sample during the treatment.

The qualities of interest

The qualities of interest can be described by suitable functions according to the theory of irreversible thermodynamics processes [1, 2].

The case of thermal treatment

The function *reaction co-ordinate* is defined as a measure for the development of a conversion process [4]. Also, the grain size is defined as a sign for the degree of order of the system and depends on the degree of irreversibility of the treatment process. On the other hand, the degree of the irreversibility of the process is described by the entropy (average) generation in the system [4, 5]. The relationship grain size – average entropy generation for a system under consideration can be determined only experimentally (empirically described). Hence, the chemical purity can be obtained (numerically) directly by the reaction co-ordinate whereas the grain size – indirectly by the average entropy generation. In this respect, empirical equations have been built using experimental data – Scanning Electron Microscopy (SEM) for the grain size and Differential Scanning Calorimetry (DSC) and Thermal Gravimetry (TG) for the entropy generation. Since the qualities of the final product are what we are interested in, the final values of the functions are needed: final reaction co-ordinate (FRC) and final average entropy generation (FAEG).

The experimental techniques used to obtain the qualities of interest and evaluate the thermodynamic functions are presented in tab. 1.

Table 1. Experimental techniques for investigation of the qualities of interest and thermodynamic functions

Treatment type	Material	Quality-of-interest	Experimental technique used	Thermodynamic function of interest	
				Name	Symbol
Thermal	$LiCoPO_4$	Chemical purity	X-ray diffraction	Final reaction coordinate	ξ_{fin}
Thermal	$LiCoPO_4$	Grain size	Scanning electron microscopy	Final average entropy generation	$\bar{\sigma}_{\text{fin}}$
Mechanical	$PdSe_2$	Transition order	X-ray diffraction	First partial derivative of the adjusted thermodynamical potential	$\frac{\partial g}{\partial p}{}_{\text{T}}$
Mechanical	$PdSe_2$	Degree of stability	X-ray diffraction	Entropy generation	σ_{gen}

The FRC ξ, eq. (3), and the FAEG $\bar{\sigma}_{\text{fin}}$, eq. (4), for the case of thermal treatment were computed on the base of DSC-TG experimental data in non-isothermal/isothermal regime for fixed heat rates [1, 2]:

$$\xi \quad {}_{i}\, \frac{\Delta h}{\Delta h_{\text{tot}}} \tag{3}$$

and

$$\bar{\sigma}_{\text{fin}} \quad w_{i} \quad \frac{c_p}{T}{}_{i} \tag{4}$$

The DSC-TG analyses were carried out using DSC-TG analyser Calvet 111, SETARAM, consisting of microbalance B111 and calorimeter DSC111. The grain size of the final product was analysed by SEM technique using JSM-6400F microscope. The morphological parameters were evaluated on the base of SEM images with the Image Tool free software. The chemical purity of the final product was analysed by X-ray difractometry (XRD) technique using a Brucer D5000 diffractometer in the Bragg--Brentano geometry with Cu anti-cathode: $K_{\alpha 1}$ = 1.540598 Å and $K_{\alpha 2}$ = 1.54439 Å. The power was 40 kV/30 mA with data collection obtained by a linear detector.

The case of mechanical treatment

The order of the transition process is defined by the order of thermodynamic potential partial derivative, which is discontinuous function [1]. First order transition means that the parameters are changed by a leap. Second order transition means gradual change of the parameters. The degree of stability of a current state indicates its remoteness to the equilibrium state [1]. On the other hand, the higher the entropy generation in the system, the remoter the current state from the equilibrium is. In this regard, the degree of stability of a given state can be described by the entropy generation in the system. The relationship degree of stability/entropy generation can be determined only experimentally. The transition order can be obtained directly by the calculation of the first derivative of the thermodynamic potential (TDPFD) and the degree of stability – indirectly by the entropy generation (EG). The experimental techniques used to obtain the qualities of interest and evaluate the thermodynamic functions are represented in tab. 1.

The TDPFPD ($\partial g/\ p$), eq. (5), and the EG σ_{gen}, eq. (6), for the case of mechanical treatment, were computed on the base of the experimental data for pressure and specific volume, collected by XRD under beam-line ID30 in the ESRF:

$$\frac{\partial g}{\partial p}_{\mathrm{T}} \quad v \tag{5}$$

and

$$\sigma_{\mathrm{gen}} \quad \frac{1}{T}\frac{\mathrm{d}}{\mathrm{d}t} \, {}^{p}_{p_0} \, v\mathrm{d}p \tag{6}$$

Results and discussions

The case of thermal treatment

Figure 3 represents the behaviour of the current average entropy generation (CAEG) during the thermal treatment at four fixed heat rates. Two regime parameters characterize its behaviour: the heat rate and the plateau duration. When the heat rate increases, the CAEG and the process irreversibility increase as well. In plateau duration the CAEG decreases diminishing the process irreversibility, accumulated during the temperature increase. Let us remind the fact that the final product with very small grains can be obtained at strongly irreversible treatment process. Therefore, if one likes to obtain as smaller grains as possible, the process of temperature increase must be as fast as possible and the plateau duration must be as shorter as possible.

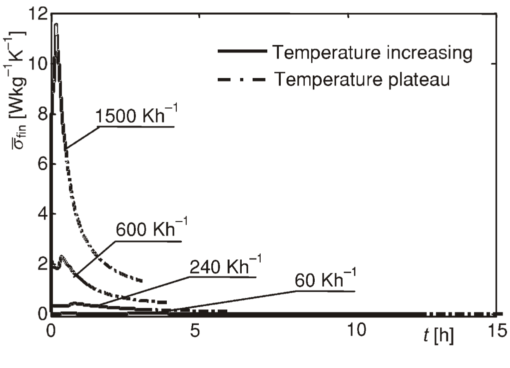

Figure 3. Current average entropy generation *vs.* time

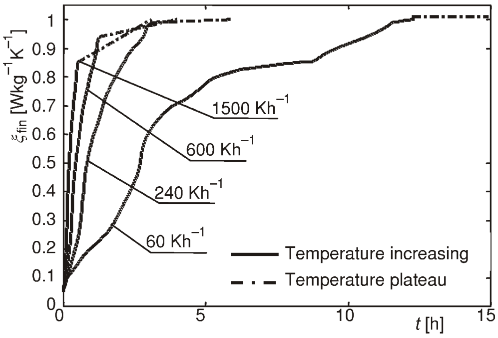

Figure 4. Current reaction co-ordinate *vs.* time

The behaviour of the current reaction co-ordinate (CRC) during the thermal treatment regime at four fixed heat rates is presented in fig. 4. It is characterized by the same regime parameters as the entropy generation. The increase of the heat rate causes CRC to decrease in the end of the temperature increase part. If plateau is applied it leads CRC to increase, since the higher the heat rate the longer the plateau duration is needed to terminate the reaction (to have reaction co-ordinate equal to 1). Therefore, to complete the reaction (pure final product) it is necessary either slow temperature increase or to apply plateau, which in any case means weak irreversible process.

If we summarise the constrains on the entropy generation (requirements to determine the grain size of the final material) and the reaction co-ordinate (requirements to determine the chemical purity of the final product) a contradiction between them can be revealed. The small grain size requires strongly irreversible process whereas the high purity – weakly irreversible one. Therefore, a compromise should be fulfilled to satisfy the constraints. To find out the optimal regime parameters it is necessary additional experiments to be done (to prepare final product in thermal regimes by temperature increase in several fixed heat rates) to obtain exact description of the relationship between the grain size and the entropy generation.

Mechanical treatment

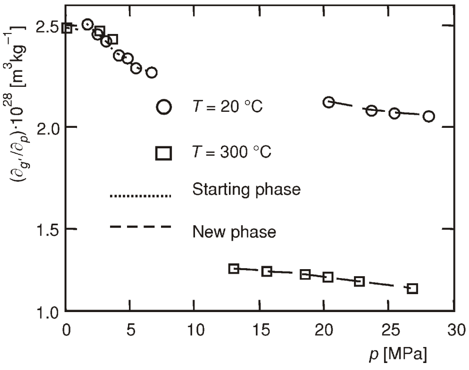

Figure 5. Thermodynamic potential first patial derivative *vs.* pressure at environmental temperature

The behaviour of the first partial derivative of the TDPFPD during the compression process at two fixed temperatures is presented in fig. 5. The TDPFPD is discontinued at both temperatures, which means that the transition process is first-order one. The temperature influences on the discontinuity point (the transition point) as follows: the higher the temperature, the lower the transition pressure is. One more, a very interesting impact of the temperature is observed: the higher the temperature, the bigger the discontinuity is. In other words, this means that the first-order character of

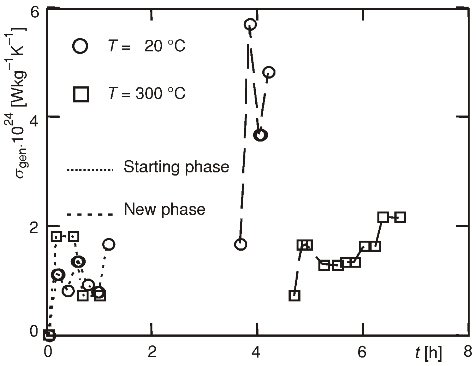

Figure 6. Entropy generation *vs.* time at environmental temperature

the transition process is stronger. The behaviour of the EG during the compression process at two fixed temperatures is presented in fig. 6. The EG decreases only during the first few minutes of the compression. The increase of the pressure causes an increase of the EG and hence a decrease of the degree of stability of the material.

The EG decreases in the transition point with a leap. This stands for: (1) The new phase has higher degree of stability in the transition point than the original one. This explains the occurrence of the transition; (2) The EG, similar to the first partial derivative of the thermodynamic potential, is discontinuous in the transition point and can be used as a criterion for the transition order. The fact that the discontinuity of the EG is bigger at higher temperature shows that the transition process is facilitated at higher temperature. An evaluation of the EG of the new phase (after the transition point) shows that the new phase has lower EG at higher temperature. In this respect, it can be asserted that the new phase is more stable (has higher degree of stability) at higher temperature. Therefore, to obtain sufficiently stable new phase (stable under atmosphere pressure), the compression process must be realised under sufficiently high temperature. Additional experiments are required, to obtain new phases by compression at several fixed temperatures, to find out which temperature is sufficiently high and to obtain an exact formulation of the relationship between the new phase degree of stability and the entropy generation in the process

Experiments to establish the relationship between the thermodynamic functions and the qualities of interest

Thermal treatment

Powder $LiCoPO_4$ was synthesised for four fixed plateauless thermal regimes. The qualities of the final product were analysed by XRD and SEM. The FAEG and the FRC were computed on the base of DSC-TG measurements. The characteristics of the applied thermal regimes and obtained qualities of interest are presented in tab. 2. As can be seen, all products obtained in plateauless thermal regimes, are out of the domain of interest. They are either with rather big grains, or impure. This observation leads to the conclusion that it is not possible to prepare a pure product with small enough grains in plateauless thermal regime. Anyone would ask the question: “Why is this not possible?”. The answer is that if the heating is slow enough to ensure sufficient reaction co-ordinate

Table 2. Regime and thermodynamic parameters, final grain size and chemical purity

N	Heating regime parameters			Thermodynamic parameters		Qualities-of-interest parameters		
						Grain size		Chemical purtity
	T_{max} [°C]	w [Kh^{-1}]	t_{plat} [h]	$\bar{\sigma}_{fin}$ [$Wkg^{-1}K^{-1}$]	ξ_{fin} [$kgkg^{-1}$]	d_{agg} [μm]	d_s [μm]	–
	–			by DSC-TG		by SEM		by XRD
1	750	60	0	0.010	1.00	20	8.0	No impurities observed
2	750	240	0	0.190	0.99	16	1.5	No impurities observed
3	750	600	0	1.189	0.94	14	0.4	Some impurities observed
4	750	1500	0	6.596	0.85	10	0.2	Impurities observed

(to serve the chemical conversion process), a few number of nuclei is originated. This ensures conditions for untroubled growth of the single crystals. Naturally, the final product is built of rather big grains. In the opposite case, if the heating is fast enough to ensure large number of nuclei to originate and respectively, to avoid consolidation the single crystals, the FRC is too low, because the conversion process is too much troubled. Obviously, the contradiction between the two requirements cannot be overcome without a plateau thermal regime. To satisfy these simultaneous constraints, a short duration plateau, immediately after the fast temperature increase, could be applied. The effect of the short duration plateau on the purity is to terminate the conversion process (chemical relaxation). The effect on the grain size is to terminate the single-crystal growth and to start the crystal fusion. Due to the fact that the chemical relaxation (conversion process termination) is much faster than the crystal growth, the final effect is pure product with small grains.

On the base of the experimental data (DSC-TG and SEM) of the investigated (without plateau) thermal regimes, empirical equations have been established as follows:

$$d_{agg} \qquad 1.577 \ln (\bar{\sigma}_{fin} \qquad 0.012) \qquad 13.093 \tag{7a}$$

respectively

$$\bar{\sigma}_{fin} \qquad \exp \frac{13.093 \qquad d_{agg}}{1.577} \qquad 0.012 \tag{7b}$$

and

$$d_s \qquad 0.362 \ln (\bar{\sigma}_{fin} \qquad 0.01) \qquad 0.688 \tag{8a}$$

respectively

$$\bar{\sigma}_{fin} \qquad \exp \frac{0.688 \qquad d_s}{0.362} \qquad 0.01 \tag{8b}$$

Using eqs. (7) and (8), the so-called critical value of FAEG can be determined. This is the value which the thermal regime must have in order to obtain the desired final product: grain size of $d_{\text{agg}} = 14\ \mu\text{m}$ and $d_{\text{s}} = 0.5\ \mu\text{m}$ and chemical purity of $\xi_{\text{fin}} = 0.98$. It was found to be 1.4 W/kgK.

After receiving the connection between grain size and FAEG, eqs. (7) and (8), 2-D space FAEG/FRC was investigated at four fixed heat rates, fig. 7, to reveal the influence of the thermal regime on the final qualities of interest. As can be seen, only the $\overline{\sigma}_{\text{fin}} - \xi_{\text{fin}}$ curve at the highest heat rate has a part belonging to the region of interest. It could be concluded that to receive a pure final product with small grains, only a combination of fast temperature increase followed by a short-duration plateau should be applied. It would ensure: (1) origination of a large number of nuclei (during the fast temperature increase), (2) complete chemical relaxation (during the long enough plateau), and (3) single-crystal fusion prevention (during the short enough plateau). Using eqs. (3) and (4), thermodynamic calculations have been performed to determine which combination of thermal parameters (heat rate and plateau duration) can ensure the critical value of FAEG (the desired grain size, respectively). It has been found that the so-called optimal thermal regime can be obtained at 1500 K/h heat rate and 2 h 16 min. plateau-duration with a value of FAEG of 1.4 W/kgK. To verify these results, a final product was synthesised at the optimal thermal regime and its qualities of interest were analysed. The XRD pattern showed pure product and the SEM images, figs. 8 and 9, – agglomerates with average diameter of about 14 μm and single particles of about 0.5 μm.

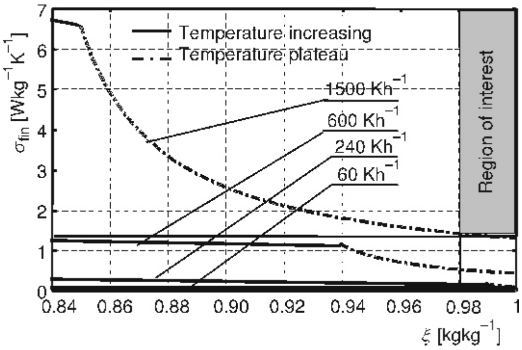

Figure 7. The 2D space FAEG/FRC for fixed heat rates

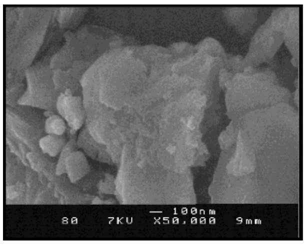

Figure 8. SEM image (agglomerates) of the test product

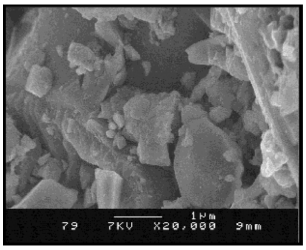

Figure 9. SEM image (single particles) of the test product

These results cover completely the predictions on the base of the thermodynamic calculations. In this respect, it can be concluded that the FAEG is very useful estimation for the grain size creation. To analyse the influence of each of the thermal regime parameters, the final product of the optimal thermal regime was compared to these of two

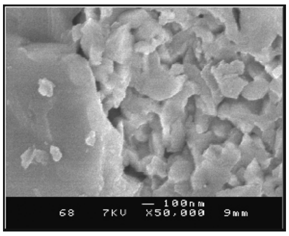

Figure 10. SEM image (agglomerates) – final product from heating regime w = 600 K/h, T_{max} = 750 °C, t_{plat} = 0 h

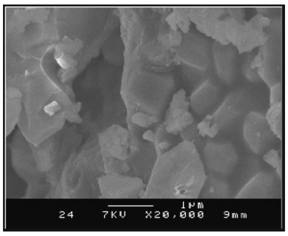

Figure 11. SEM image (single particles) – final product from heating regime w = 1500 K/h, T_{max} = 750 °C, t_{plat} = 0 h

without-plateau regimes: (1) with the same heat rate and (2) with approximately the same FAEG.

The first comparison reveals the influence of the plateau-duration, figs. 8 and 10, whereas the second – the influence of the heat rate, figs. 9 and 11. As can be seen from figs. 8 and 10, if plateau is applied, this makes the agglomerates more monolithic. Hence, the plateau-duration has an effect on the single-crystal growth and fusion. If figs. 9 and 11 are compared, one can see that at FAEG fixed, the heat rate increase causes a decrease of the single-particle size. Thus, the heat rate has an effect on the nuclei origination. These observations completely confirm the theoretical predictions.

Mechanical treatment

Unfortunately, the available equipment did not allow additional experiments to be carried out to reveal the influence of the environmental temperature and the degree of irreversibility of the compression-process on the final product degree of stability. This is the reason, these relationships not to be established empirically, and respectively, not to be determined treatment conditions to receive a new phase, stable at normal conditions. On the base of the experimental data collected, the behaviour of the $PdSe_2$ powder during compression at two temperatures fixed was described numerically. Equations were established for the relationships: thermodynamic potential – pressure, eqs. 9a and 9b, and specific volume – pressure, eqs.10a and 10b, at the two fixed temperatures. These equations can be used also to obtain the values of the transition pressure at the discussed temperatures:

$$\Delta g\ 10^{18} \quad \begin{array}{ll} 0.404\ln p \quad \dfrac{183.414}{\ln p}, & p \quad 12.240\ \text{GPa} \\ \\ 112.072 \quad 4.889\ln p, & p \quad 12.240\ \text{GPa} \end{array} \quad \text{at } T \quad 20\ \text{C} \tag{9a}$$

$$\Delta g\ 10^{18} \quad \begin{array}{ll} 0.118\ln p \quad \dfrac{40.181}{\ln p}, & p \quad 9.785\ \text{GPa} \\ \\ 51.921 \quad 2.299\ln p, & p \quad 9.785\ \text{GPa} \end{array} \quad \text{at } T \quad 300\ \text{C} \tag{9b}$$

$$\nu\ 10^{28} \quad \begin{array}{ll} 0.08\ln p \quad 4.013\ 10^{3}p^{\ \ 0.4}, & p \quad 12.240\ \text{GPa} \\ \\ 2.279-2.222\ 10^{-13}p^{1.15}, & p \quad 12.240\ \text{GPa} \end{array} \quad \text{at } T \quad 20 \quad \text{C} \tag{10a}$$

$$\nu\ 10^{28} \quad \begin{array}{ll} 0.158\ln p \quad 0.427\ 10\ {}^{2}p^{0.25}, & p \quad 9.785\ \text{GPa} \\ \\ 4.341 \quad 0.130\ln p \quad 10\ {}^{37}p^{\ 4}, & p \quad 9.785\ \text{GPa} \end{array} \quad \text{at } T \quad 300 \quad \text{C} \tag{10b}$$

Conclusions

The thermal treatment

(1) Final product with required qualities (chemical composition and morphology) can be synthesised in thermal-treatment regime, if the degree of irreversibility is defined prior to.

(2) As the chemical stress of the treated system relaxes much faster than the morphological stress, a thermal treatment regime, ensuring complete chemical relaxation (pure final product) and high morphological stress (small-grained morphology) can be created. Its parameters can be defined by analysing its degree of irreversibility.

(3) The thermal-treatment regime degree of irreversibility (entropy generation and reaction co-ordinate) can be evaluated on the base of DSC-TG experimental data. Particularly, in the case of $LiCoPO_4$:

- Pure $LiCoPO_4$ with homogeneous grain size can be synthesised in one-step thermal regime (without intermediate mixings), when the treated sample is formed in thin ($\delta = 0.5$ mm) layer.
- Pure $LiCoPO_4$ with single-particle average diameter about 1 µm can be prepared in thermal regime by heating (heat rate 1500 K/h) in argon atmosphere, from ambient temperature to 750 °C, keeping it 2 hours and quenching in air to ambient temperature.
- Pure $LiCoPO_4$, with single-particle average diameter about 3 µm, can be prepared in without-plateau thermal regime by heating (heat rate 240 K/h) in argon atmosphere from ambient temperature to 750 °C and quenching in air to ambient temperature.

The mechanical treatment

(1) The new-phase stability can be controlled by controlling the treatment process parameters. For this goal, however, a thermodynamic analysis of the treatment process must be fulfilled prior to.

(2) The increase of the environmental temperature causes not only decrease of the critical pressure, but an increase of the new-phase stability as well.

(3) The thermodynamic behaviour (transition pressure, thermodynamic potential, specific volume) of the material during mechanical treatment at isothermal conditions can be described numerically on the base of XRD experimental data, generated by synchrotron radiation.

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Nomenclature

Bi – Biot number, [–]
c_p – specific heat capacity, [J/kgK]
d – average diameter, [μm]
g – thermodynamic potential (Gibbs free energy), [J/kg]
h – specific enthalpy, [J/kg]
l – length, [mm]
p – pressure, [GPa]
T – temperature, [°C]
t – time, [h]
v – specific volume, [m^3/kg]
w – heating/compression rate, [K/h]

Greek symbols

α – convection heat transfer coefficient, [W/m^2K]
Δ – change, [–]
δ – thickness, [mm]
ξ – reaction co-ordinate, [kg/kg]
λ – heat conductivity, [W/mK]
σ – entropy generation, [W/kgK]
ϕ – diameter, [mm]

Superscripts

w=max – maximal heating rate
adj – adjusted

Subscripts

agg – agglomerate
conv – convection

crit – critical
fin – final
gen – generated
incr – increase
max – maximal
p – at constant pressure
plat – plateau
rad – radiation
s – single particle
T – at constant temperature
tot – total

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