platinum wire in an electro-thermographic cell, i.e. under the conditions, where the high degree of uniformity of the external parameter fields is ensured. The structure arises as a result of disintegration of a uniform mode in the deep diffusion region; in this case the domain is overheated to temperatures exceeding significantly those in the diffusion region, which were treated in the classical kinetics as the maximum possible.

The same paper describes various self-oscillatory, spatially nonuniform regimes in ethylene oxidation in the catalytic cell of an electro-thermograph. The oscillatory process shows itself up as a pulsatory change in the location of the boundaries demarcating the zones of the hot and cold domain. The researcher, who is unaware of the possibility of stratification of the process and observes oscillations by the integral signal, would traditionally describe these phenomena in terms of homogeneous moels, which would, obviously, have no relation to the actual kinetics. The kinetic studies on heterogeneous catalysis quote a great many of examples of an oscillatory instability in the conversion regimes being interpreted in terms of homogeneous models, but none of them contains an analysis of the spatial patterns of these phenomena.

The paper (VOLODIN, BARELKO, 1983) presents data on stratification in conversion processes due to factors of electrochemical nature. These phenomena are most typical of the kinetic measurements using as sensitive elements incandescent filaments and should be taken into consideration in their interpreting. As known, such sensitive elements are widely used in the cells of the kinetic devices intended for studying various catalytic and adsorption-desorption processes.

Unfortunately, at this stage the kinetics of heterogeneous catalytic reactions as a whole remains within the limits of the classical approach operating with homogeneous schemes and models. The studies aimed t working cut new apparats of the kinetic theory and new experimental approaches in investigating the kinetic features of chemical conversions with due regard to the transfer factors are still few. It may be stated that in this respect the chemical kinetics is far behind the physical kinetics that is greatly involved in studying self-organization phenomena in various systems, such as plasma, semiconductors, biologically active media and other fields.

NON-STATIONARY NUCLEATION AND THE JOHNSON-MEHL-AVRAMI EQUATION

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1. Introduction

Phase transitions frequently proceed via the formation and growth of clusters of a newly evolving phase in the initially metastable homogeneous medium.

In the interpretation of experimental investigations of such processes often the classical nucleation theory is used (BECKER, DÖRING, 1935; AVRAMI, 1939, 1940, 1941; FRENKEL, 1946; GIBBS, 1906; ZELDOVICH, 1943; VOLMER, WEBER, 1926). This theory contains a number of restrictive assumptions like the following:

- The microscopic structure of the clusters is identical to the structure of the stable phase in macroscopic dimensions

- The specific surface energy of the cluster in the medium is equal to the value corresponding to a planar interface between both phases (and is only slightly temperature dependent)

- The clusters are of spherical shape

- The evolution of the cluster distribution is the result mainly of reactions between clusters and monomers

- The contribution to the energy of cluster formation due to translational and rotational degrees of freedom is negligible

- The thermodynamic constraints and the supersaturation are kept constant in the course of nucleation resulting after some time-lag τ in the establishment of a steady-state nucleation rate I_∞.

In experimental investigations in many cases as a first step not the cluster distribution but the volume fraction x of the newly evolving phase is measured as a function of time. The application of the classical nucleation theory leads to the following expression for x(t) (AVRAMI, 1939, 1940, 1941; JOHNSON, MEHL, 1930)

$$x(t) = 1 - \exp\left\{ - \frac{\pi}{3} I_\infty g^3 t^4 \right\} \qquad (1)$$

Eq. (1) is usually denoted as Johnson-Mehl-Avrami equation (JMA).

To be definite, here the crystallization in melts is considered. The growth rate of the clusters is denoted by g, it is assumed to be limited by reactions at the surface of the cluster (reaction limited growth).

If both the nucleation rate I and the growth rate g are time-dependent due to time-lag effects, to time-varying constraints or variations of the state of the medium in the course of the transition, then x(t) has to be calculated from a generalized JMA-equation (CHRISTIAN, 1975)

$$x(t) = 1 - \exp\left\{ -\frac{4\pi}{3} \int_0^t I(t') \left[\int_{t'}^{t} g(t'')dt'' \right]^3 dt' \right\} \qquad (2)$$

In the present paper the influence of a time dependence of the nucleation rate on x(t) is analyzed which is due to time-lag effects and to well-defined variations of the temperature in the course of the transition. The non-steady character of the nucleation process implies, that the classical steady-state nucleation rate cannot be applied. It is replaced here by a kinetic approach described in chapters 2 and 3. In chapter 4 eq.(2) is applied to the calculation of time-temperature-transformation (TTT)-diagrams for a isoconcentration crystallization of a metallic melt. The results are compared with the curves obtained on the basis of the classical nucleation theory.

2. Kinetic Model and Mathematical Description

Neglecting possible spatial inhomogeneities the course of the phase transition may be described via the distribution function with respect to cluster sizes N(j,t) in dependence on time. In accordance with the assumptions underlying the classical nucleation theory the evolution of this distribution is determined by addition or evaporation of monomers. Moreover, homogeneous nucleation is assumed.

Processes of heat conduction are expected to proceed rapidly compared with the characteristic growth rates of the clusters. As a consequence at each moment a well-defined value of the temperature can be attributed to the system. Based on these assumptions the following system of rate equations may be formulated for the description of the time evolution of the cluster size distribution N(j,t)

$$\frac{d}{dt} N(j,t) = I(j-1,t) - I(j,t) \qquad (3)$$

with

$$I(j,t) = w^+(j,t)N(j,t) - w^-(j+1,t)N(j+1,t) \ . \qquad (4)$$

In a system with conservation of the particle number the actual number of monomers is calculated from

$$N(1,t) = N(1,0) - \sum N(j,t) \cdot j \qquad (5)$$

$w^+(j)$ and $w^-(j)$ are the transition rates of clusters with size j in clusters with size (j+1) and size (j-1), respectively. It means that they are the rates of attachment or detachment of a single particle. It should be mentioned, that $I(j_{cr})$ corresponds to the nucleation rate in the classical nucleation theory. The critical cluster size j_{cr} is defined by $w^+(j_{cr}) = w^-(j_{cr})$.

The application of the system of rate equations to a special system takes place by fixing the initial and boundary conditions and determining the kinetic coefficients w^+ and w^-. In most cases it is easier to find a expression for w^+ than for w^- because the decay of a cluster arises from internal processes. That is the reason for that usually the principle of detailed balance is applied to calculate w^- from a known w^+ and from the equilibrium distribution N°(j). With

$$N°(j) = N(1) \exp\left\{ -\frac{\Delta G(j)}{kT} \right\} \qquad (6)$$

we obtain

$$w^-(j) = w^+(j-1) \exp\left\{ \frac{\Delta G(j)-\Delta G(j-1)}{kT} \right\} \qquad (7)$$

k is Boltzmanns constant and $\Delta G(j)$ is the change of Gibbs free energy in the system caused by the formation of a cluster of size j. In the classical nucleation theory ΔG is expressed by a volume and a surface contribution:

$$\Delta G(j) = \Delta g \cdot j + A(j) \cdot \sigma \ . \qquad (8)$$

A(j) is the surface area of the cluster and proportional to $j^{2/3}$. Δg is the difference of Gibbs free energy per particle between initial phase and newly evolving bulk cluster phase. σ is the surface tension and is regarded as size independent. The determination of the thermodynamic driving force Δg of the phase transition for different situations is carried out in paragraph 3.

The rate of attachment of monomers to clusters of size j can be determined both for diffusion limited and reaction limited growth. In the first case one obtains from the 1. Fickian law under the assumption of a stationary concentration profile of segregating particles

$$w^+(j) = (48\pi^2/c_a)^{1/3} \, Dc_i \cdot j^{1/3} \qquad (9)$$

while for reaction limited growth the following expression holds (KELTON et al., 1983)

$$w^+(j) = 24 \frac{D}{\lambda^2} j^{2/3}$$ (10)

c_-, c_1^- in eq.(9) are concentration of segregating particles and of monomers sufficiently away from the cluster, D is the diffusion coefficient of the particles in the medium.

The basic mechanism, resulting in eq.(10), is a thermally activated jump from matrix to cluster phase at the surface of the cluster with a characteristic length λ.

The temperature dependence of D is given by a Vogel-Fulcher expression

$$D = D_0 \exp\left\{ - \frac{E_D}{k(T-T_v)} \right\}$$ (11)

E_D is the activation energy for a diffusion jump and T_v is an empirical lower limiting temperature.

In order to solve the system of rate equations (eqs.(3) to (5)) numerically a simulation technique suggested by KELTON et al. (1983) was used. They use the boundary condition

$$N(j,t) = 0 \quad , \quad j > j*$$ (12)

where j* is the largest cluster size for which N(j,t) is calculated from a rate equation. j* is equal to the number of equations of the system and limited by the computer time. The growth of clusters, consisting of more than j* particles is described by a growth equation of the general form

$$g(j) = w^+(j) - w^-(j) \; .$$ (13)

The initial distribution is given by

$$N(j,0) = 0 \quad , \quad j > 1$$ (14)
$$N(1,0) = N_1 \; .$$ (15)

If a quench of a melt from melting temperature T_m to room temperature is considered, the simulation starts somewhat below of T_m since at T_m the critical cluster size diverges. In this case the stationary distribution belonging to this temperature is used as the initial distribution.

3. The Thermodynamic Driving Force of the Transition

The determination of the evaporation rates requires the knowledge of the thermodynamic driving force Δg of the phase transition. For a

crystallization process with polymorphic transition under a constant pressure p the driving force is determined by the degree of undercooling $\Delta T = T_m - T$, where T_m is the melting (crystallization) temperature and $T < T_m$ the actual value of the temperature. In this case the difference of the Gibbs free energy per particle Δg in the solid and liquid phases, respectively, can be expressed through the difference of the molar entropies ΔS and the Avogadro number N_a via

$$\Delta g(T) = - \frac{1}{N_a} \int_{T_m}^{T} \Delta S(T')dT' \; .$$ (16)

A Taylor expansion of $\Delta S(T)$ yields

$$\Delta g(T) = - \frac{qaT}{N_aT_m} \left\{ 1 - \frac{\Delta C_p(T_m)}{2aS(T_m)} + \frac{\Delta C_p(T_m)}{2aS(T_m)} \cdot \frac{T}{T_m} \right\}$$ (17)

q is the molar heat of the transition (q>0) and ΔC_p the difference of the heat capacities in both considered phases.

For metallic melts often the relation $(\Delta C_p/\Delta S) \approx 1$ is experimentally found to be fulfilled (GUTZOW, PENKOW, 1987). In this approximation eq. (17) is reduced to

$$\Delta g(T) = - \frac{q}{N_a} \cdot \frac{\Delta T}{T_m} \cdot \frac{\Delta T}{2T_m} \; .$$ (18)

4. Isoconcentration Crystallization from a Metallic Melt

A very suitable method to give a clear idea of the temperature dependence of the kinetics of a liquid/solid transition is a TTT-(time-temperature-transformation) curve. Fig. 1 shows a calculated TTT-curve of $Au_{80}Si_{20}$ for $x=10^{-4}$. The points of the curve correspond to the time after which at constant temperature a volume fraction of 10^{-4} is transformed into the new phase. The curves in Fig. 1 differ from each other in dependence on their level of description of nucleation. If nucleation is described by the classical steady-state nucleation rate (BECKER, DÖRING, 1935; AVRAMI, 1939, 1940, 1941; CHRISTIAN, 1975; KASHCHIEV, 1969)

$$I_s = w^+(j_{cr}) \left(\frac{\Delta g}{6\pi kTj_{cr}} \right)^{1/2} \cdot N_1 \cdot \exp\left\{ - \frac{\Delta G(j_{cr})}{kT} \right\}$$ (19)

(dashed curve in Fig. 1) and if additionally the volume of the critical nuclei is taken into account in the JMA-equation

$$x(t) = 1-\exp\left\{ -\frac{\pi}{3} I_s t[g^3t^3 + 4\tau_{cr}^3 + 6\tau_{cr}^2 gt + 4\tau_{cr} g^2t^2] \right\}$$
$$\approx 1-\exp\left\{ -\frac{\pi}{3} I_s t[4^{1/3}\tau_{cr} + gt]^3 \right\} \tag{20}$$

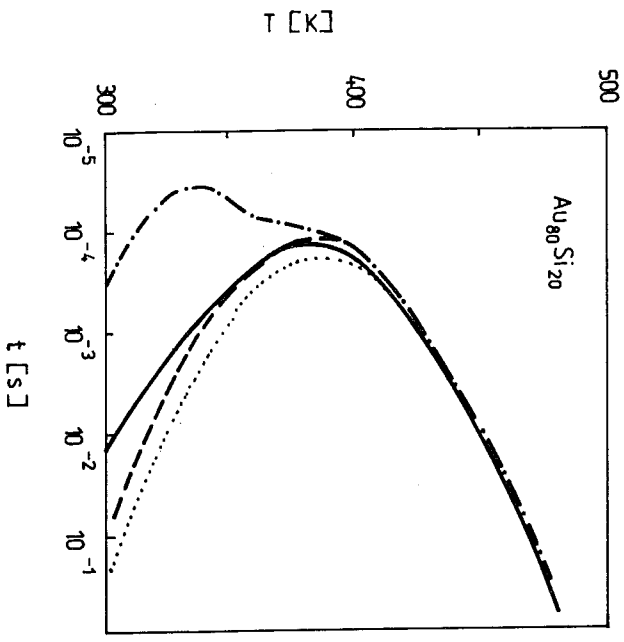one obtains a new maximum in the TTT-curve (dashed-dotted curve).

Fig. 1: TTT-plot for different approximation levels of the JMA-equation
Eq.(1) (— — — —), eq.(20) (— — — —)
Eq.(2) (··········), eq.(21) (—·—·—·—)
Parameters following KELTON, GREER (1986).

This maximum is located at the same temperature as the maximum of the stationary nucleation rate obtained from eq. (19) (see Fig. 2).

The additional maximum occurs only at high nucleation rates like those observed during crystallization in metallic melts. Taking into account additionally to the volume of the critical nuclei the existence of a non-stationary transient phase for nucleation one obtains another curve (full line in Fig. 1) using the numerically calculated rate $I(j_{cr},t)$ and the generalized form of the JMA equation

$$x(t) = 1-\exp\left\{ -\frac{4\pi}{3} \int_0^t I(t')\left[r_{cr} + \int_{t'}^t g(t'')dt'' \right]^3 dt' \right\} \tag{21}$$
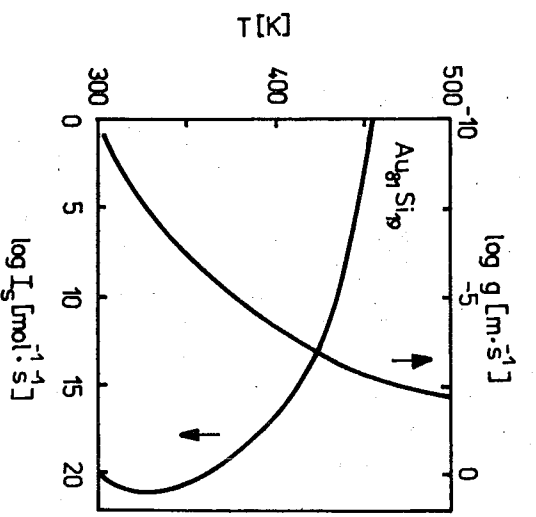

Fig. 2: Temperature dependence of the stationary nucleation rate I_s and the deterministic growth velocity g. Parameters see Fig. 1.
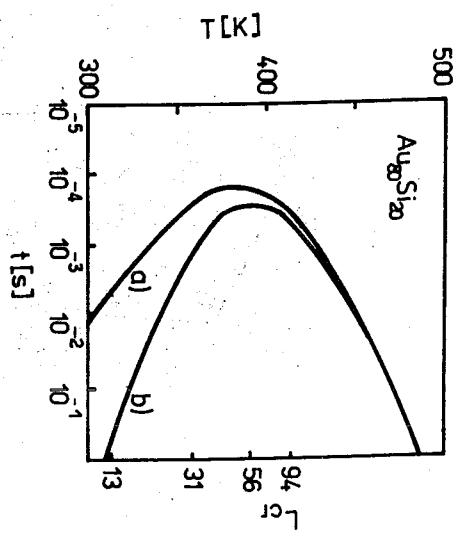

Fig. 3: TTT-plot from the improved JMA-equation (21) using numerically calculated non-stationary nucleation rates. Cristalline volume fraction $x=10^{-4}$. Cristalline phase consists of all nuclei with $j>j_{cr}$ (curve a) or with $j>300$ which is assumed to be the lowest detectable cluster size (curve b). ($L_{cr}=j_{cr}$.)

It can be seen that both additional effects — arising from the consideration of the volume of the critical nuclei and from time-lag in nucleation - compensate each other to a large extent.

The reason for this compensation is the increasing with decreasing temperature time-lag in nucleation rate caused by the decreasing

particle mobility which is proportional to $\exp(-E_2/kT)$. This is the reason why the high stationary nucleation rates at low temperatures do not have a significant effect and the contribution of the new phase volume, transformed with this rate is less important. A surprising coincidence arises with the "classical" TTT-curves calculated from eq. (1) (dashed line in Fig. 1). Fig. 1 illustrates the cause of this coincidence. In Fig. 3 both TTT-curves demonstrate a further, more practical, effect of non-stationary behaviour. The original JMA-theory adds all overcritical clusters to the new phase. In contrast, experimentally only clusters larger than a certain, fixed, size, the resolution limit of the experimental device, are registrated. Normally, this cluster size is larger than the critical size. However, the length of the time-lag in stationary nucleation rate is strongly dependent on the size of the considered nuclei. If $x(t)$ is obtained from the improved JMA-equation (21) using the numerically calculated nucleation rate of a larger, fixed cluster size (in this case $I(t,j=300)$), the TTT-curve is clearly shifted to the right compared with the curve calculated with $I(t,j=j_{cr})$. This effect increases with a decreasing temperature, that means with a growing influence of the time-lag. This has to be taken into account in the analysis of measurements with the help of the JMA-theory in order to obtain correct kinetic parameters of the process.
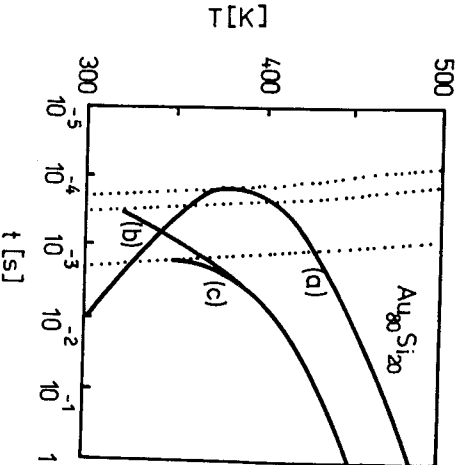

Fig. 4:
Non-stationary TTT-plot (a) compared with stationary (b) and non-stationary (c) CCT-plot for $Au_{80}Si_{20}$ and $x=10^{-6}$. The dotted lines are the linear $T(t)$-curves of the critical rates. Parameters see Fig. 1.

If, in a further step, we want to investigate $x(t)$ during the

quench of a melt from T_m to room temperature, we have to note that I and g become time-dependent because of their temperature dependence (Fig. 2) and only eq. (21) enables a correct description. To describe the crystallization behaviour one changes over from the isothermal TTT-curve to a CCT (continuous-cooling-transformation)-curve for a linear cooling law. The CCT-curve breaks off at a critical quench rate T_{cr}, by which a crystalline volume fraction $x=10^{-6}$ is frozen in. That means T_{cr} is the minimum quench rate to get a glassy state, following the criterion of UHLMANN (1972). Fig. 4 shows the numerically calculated TTT-curve for $Au_{80}Si_{20}$ (curve a), the CCT-curve from the temperature dependent stationary nucleation rate (b) and the CCT-curve from the numerically calculated nucleation rate (c) and the pertinent critical quench rates. At high T the nucleation rate does not reach the stationary value corresponding to the actual system temperature according to eq. (19) (KELTON, 1986; RICHTER et al., 1987). The reason is that the development of the cluster distribution proceeds over matter transport processes. But these transport processes are too slow compared with the temperature change to establish the stationary distribution corresponding to the actual temperature at each time. Caused by the reduced nucleation which is obtained if non-stationary effects are considered, less volume is crystallized at room temperature than we would have expected on the basis of the classical stationary nucleation rate. The non-stationary CCT-curve breaks off at lower T than the stationary one, so that T_{cr} decreases by a factor of the order 10. All this follows from the abolition of the last restrictive assumption in paragraph one.

5. Summary

The variation of thermodynamic constraints during crystallization of a melt leads to some new effects which cannot be described by classical nucleation theory. The solution of the system of rate equations for the evolution of the cluster size distribution with parameters corresponding to special representative systems results in the follow-ing differences to classical nucleation theory:

1. Isothermal TTT-curves for metallic melts calculated from the JMA-equation show a significant shift at lower temperatures if the non-stationary initial phase or the volume contribution of critical nuclei to the new phase is taken into account. Both shifts compensate each other partially.

2. An interpretation of experimental $x(t)$- or TTT-curves has to take

into consideration that only nuclei larger than the resolution limit contribute to the transformed volume fraction which is measured and not as assumed in classical nucleation theory all nuclei larger than the critical size. The cluster-size-dependent time-lag in nucleation rate shifts the TTT-curve to significant larger times.

3. During rapid quenching of a melt the nucleation rate cannot reach the stationary value corresponding to the actual temperature of the system. After quenching less nuclei are frozen in as this would follow from the classical theory. This leads to a considerable reduction of the critical quench rate in metallic melts.

RANDOM WALKS ON FRACTALS

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1. Introduction

In recent years, there has been an increasing interest in the study of systems with fractal time or space properties (for a recent review, see HAVLIN, BEN-AVRAHAM, 1987). One of the reasons for this interest is that systems with disorder possess the dilatation symmetry characteristic for fractals. A famous example is the percolating cluster. One can thus hope that a study of fractal systems will lead to a better or new understanding of systems with disorder. The fractals that arise in this and other contexts (such as in diffusion limited aggregation, porous media, etc.) are usually random fractals, and an analytic study is very difficult. However, some progress can be made when one restricts oneself to the study of deterministic fractals, which one can try to construct such as to mimic as closely as possible the more complicated random fractals.

Here, we will investigate a basic dynamical property on simply connected deterministic fractals, namely the first passage time to go from the point at the origin to one of the sites lying at large distance from this point. As far as we know, all the previous exact dynamical results deal with moments of some quantity (usually the mean square displacement) whereas the technique presented here allows the calculation of a probability density, namely the first passage time density.

One ingredient of our technique is the derivation of a renormalization equation in the same way as was done by MACHTA (1981) for a random walk in one dimension. The second ingredient is the introduction of an auxiliary function f, defined in a unique way as the solution of a functional equation of the following type:

$$p(f(x)) = f(ax) \qquad f(0) = f'(0) = 1 \qquad (1)$$

The detailed form of p depends on the (site and bond) geometry of the fractal under consideration. Using the function f, one can reduce the renormalization equation to a simple form which can be solved by iteration. It is also hoped that the introduction of such an auxiliary function may be useful to solve renormalization equations arising in