Journal of Thermal Analysis, Vol. 32 (1987) 1645–1650

THERMODYNAMICS AND THERMOCHEMISTRY OF KINETIC (REAL) PHASE DIAGRAMS INVOLVING SOLIDS

J. Šesták and *Z. Chvoj*

INSTITUTE OF PHYSICS, CZECHOSLOVAK ACADEMY OF SCIENCES,
NA SLOVANCE 2, 180 40 PRAGUE 8, CZECHOSLOVAKIA

A theoretical analysis of the formation of materials with metastable microstructures under non-ideal and highly non-equilibrium conditions is presented.

The most important processes in material engineering include crystal growth or dissolution from multicomponent (usually high-temperature) solutions. Selection of the most suitable conditions for obtaining a controlled type of crystalline (or even non-crystalline) materials requires a good knowledge of the heterogeneous equilibria between the solid and liquid phases, conveniently collected graphically in the form of phase diagrams. The most widespread are those diagrams describing the equilibrium dependence of the composition upon the temperature, but this is not easy to achieve experimentally [1]. In technology we can practically control or present (or often leave undefined) many parameters as follows:

— Chemical and physical properties of the sample (composition, compactness, homogeneity, impurity, diffusivity, viscosity or even prenuclei sites or mechanical tensions).

— External forces (temperature, pressure, partial pressure, or electromagnetic, hydrostatic or gravitational force fields) and their changes (heating or cooling, convection, atmospheric composition and hydrodynamics and associated flows).

— Sample geometry, including the factors affecting the heat exchange, sink and generation, the extent of volatile component exchange, the interactions between interfaces and/or with the surroundings or with the measuring head.

Furthermore, the classical approach to the study of phase equilibria by long annealing at increased temperature is generally found to be tedious and experimentally demanding. Therefore, dynamic techniques are often preferred as more convenient, in which the tempered sample is investigated in the freeze—in state after a suitable rapid quenching and/or during the entire programmed cooling. A detailed consideration of all the peculiarities involved in such a non-equilibrium procedure is definitely required. It can be verified that for fast enough processes,

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

occurring, for instance, in metals and alloys, near-equilibrium conditions can be assumed even at the relatively high cooling rate of 10^2 degree s^{-1}, whereas for the very slow diffusional or viscous processes in silicate systems the cooling rate must be as low as 10^{-4} degree s^{-1}, and to avoid undercooling (or even limiting glass-formation) equilibration of the order of weeks may be required.

To look for materials with desired (specific) properties, we certainly have to use phase diagrams which correspond to non-equilibrium conditions of their preparation, which provide us with the necessary information of possible thermodynamic stability, metastability and even instability under the assumed standard (equilibrium) conditions. There is increased interest in the mathematical analysis and synthesis of such "kinetic" phase diagrams. Besides the classical requirements if the minima and equality of the Gibbs energies of the individual components of the coexisting stable phases, we have to assume the same for the metastable phases occurring at higher energy levels (and different compositions) than for the stable phases, the latter not being achieved due to the kinetic hindrance of new phase formation (nucleation). For the sake of practical use, metastable boundaries can be predicted by a simple extrapolation of the coexistence lines for the stable states into non-equilibrium regions, usually down to lower temperatures. Alternatively, the preliminary shapes of metastable lines can be estimated from a superposition of two corresponding (e.g. simple eutectic) phase diagrams [2]. This is of considerable importance for all dynamic methods (from thermal analysis to sample quenching) for the correct interpretation of the phases observed.

For a system which cannot follow the experimentally enforced (strong) changes, even by establishing the previously discussed metastable equilibria, the boundary lines shift freely along both the concentration and temperature axes, forming thereby the regions of unstable phases to be described in terms of the kinetics of the physico-chemical processes. Such a truly kinetic phase diagram is fully dependent upon the experimental conditions applied (cooling rate, sample geometry and measuring conditions) and can be best treated mathematically in the case of a stationary process conditioning. Paper [6] summarizes the results attained in this field by using the solution of the kinetic equations (Focker–Planck equation) or the Monte-Carlo method. The new method for the description of kinetic phase diagrams based on the stochastic process theory [7, 10] enables us to describe non-stationary processes too. These include such phenomena as "coring" and "surrounding" (see (1)), known long ago in metallurgical engineering, explaining the concentration-dependences across the grains precipitated in the vicinity of hypoeutectic points, respectively.

The kinetic phase diagrams can be used for the description of the processes connected with the preparation of metallic glasses (10^3–10^7 degree s^{-1}) or with the photon, electron or ion beam processing of the surfaces of many materials. The cooling rates reached during, for example the laser glassing of metals, can be as fast as of the order of 10^{10} degree s^{-1}, yielding associated processes of phase formation that are very highly non-equilibrium.

In the case of the non-stationary processes, the composition of the solid phase changes with time as well as the local cooling rate and degree of undercooling at the phase interfaces. Mathematical treatment is then extremely difficult, requiring a joint solution of the equations for heat and mass transfer under given boundary conditions, and the kinetic equations describing the kinetics of the phase transformation on the solidification front. Evaluations under the stochastic theory yield interesting dependences between the undercooling, concentration, linear growth rate and cooling rate (see [5, 8, 10]). The results for Cu—Ni alloy and similar systems are demonstrated in Table 1. For instance, if the cooling rate R increases, the difference in the concentrations of the solid and the liquid phase decreases and tends to zero. This result can simulate the creation of the amorphous phase during rapid cooling.

Not less important in the theoretical treatment is the thermochemistry of mixtures and solid solutions. For example, with regular solutions ($\Delta H^{ex} \gg T\Delta S^{ex}$), interactions decisive for the system behaviour take place between spherical species

Table 1 Qualitative dependences of the growth parameters on the kinetic properties of solidification

Change of values / Increase values	Temperature on the solidification front, T_r	Undercooling, ΔT	Concentration of the liquid phase, C_{liq}	Concentration difference on the solidification front, $C_{liq} - C_{sol}$	Growth rate of solid phase formation, G
Cooling rate, R $(10^3 \rightarrow 10^6\ Ks^{-1})$	intensive decreases	increases	decreases	decreases	nonlinear increases
Diffusion coefficient, D $(10^{-7} \rightarrow 10^{-3}\ m^2\ s^{-1})$	decreases	increases	increases	decreases	increases
Kinetic coefficient,* k $(10^6 \rightarrow 10^{1-}\ s^{-1})$	increases to equilibrium value	decreases to zero	decreases	increases	increases

* i.e. rate constant of the front solidification including thermal vibration of molecules, probability of molecules incorporation into solid phase dependent on temperature, interface energy barrier and the difference of Gibbs energy of both phases.

Table 2 Gibbs energy ΔG_{mix} ($= \Delta H^{\mathrm{id}} + T\Delta S^{\mathrm{id}} + \Delta H^{\mathrm{ex}} + T\Delta S^{\mathrm{ex}}$) for binary mixture ($A+B$) assuming different models of the system nonideality

Name	ΔH^{ex}	ΔS^{ex}
ideal	0	0
athermal	$x_A \ln (x_A + \Omega_B x_B) + x_B \ln (x_B + \Omega_A x_A)$	
regular	Q_R	0
subregular	$Q_R \cdot Q_S$	0
pseudoregular	Q_R / Q_S	0
quaziregular	$Q_R \cdot Q_K$	$\ni x_A x_B \Omega_T$
quazisubregular	$Q_R \cdot Q_K \cdot Q_S$	
quazipseudosubregular	$Q_R \cdot Q_K / Q_S$	

Where T, ΔH, ΔS, Ω and x are temperature, enthalpy and entropy change, interaction parameter and mole fraction, respectively, for ideal (id) and excess (ex) quantities. Read $\Delta H^{\mathrm{id}} = 0$, $\Delta S^{\mathrm{id}} = x_A . \ln x_A + x_B \ln x_B$, $Q_R = \Omega x_A x_B$, $Q_S = (1 + \Omega_B x_B)$, and $Q_K = (1 - \Omega_T T)$.

of (molecular) mixtures of metals (see Table 2), whereas for the decisive effect of the mutual arrangement of usually geometrically complicated species of polymers and silicates we have to take up athermal solutions ($\Delta H^{\mathrm{ex}} \ll T\Delta S^{\mathrm{ex}}$). A specific case of ionic (Temkin) solutions requires the incorporation of energetically unequal sites in the solid-state network into the above concept of regular solutions. This is usually true for oxides where, for example, energetically unequal (disparate) tetrahedral (i) and octahedral (j) sites are occupied on different levels of the species A and B, so that the ordinary term $x_A \ln x_A$ must be read as the term $\sum x_{Aij} \ln x_{Aij}$, etc.

For the sake of practical applicability, a graphical form of the above effects is shown for the case of a hypothetical phase diagram of a binary mixture of A and B. Under the conditions of ultrafast cooling, the phase boundary is depressed to lower temperatures (see Fig. 1b), to be observed experimentally later in a position not associated with that normally called the equilibrium phase boundary (Fig. 1a). If the chemical phases of the system (in Fig. 1a) change in such a way that the mixing of components A and B is accompanied by a large enthalpy change due to strong interactions between A and B solutions (see Table 2), a eutectic point [1] emerges. For still intensive interactions, a more complicated form may occur, exhibiting peritectic compound C. Such a type of phase diagram (see Fig. 1c) is illustrative to show possible consequences of phase metastability represented by dashed lines. If the solidified compositions of this system are reheated, phase boundaries corresponding to metastable phases are often observed, making correct interpretation of the experimental data difficult; this is particularly true for thermoanalytical measurements [9] (e.g. DTA).

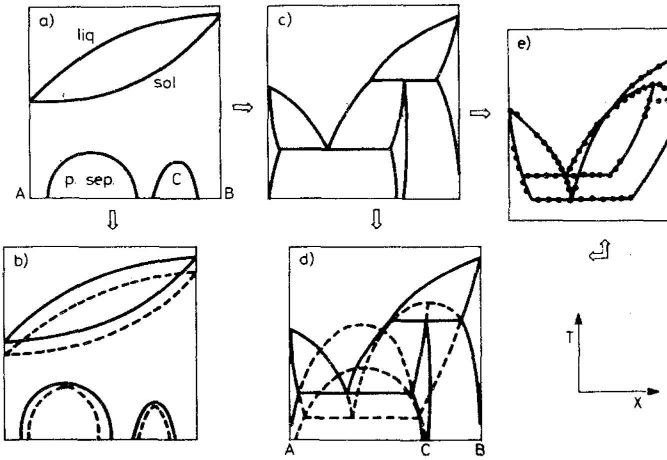

Fig. 1 Possible shifts and extrapolations in a hypothetical phase diagram of binary mixture *A* and *B*. a – near-ideal behaviour of solid-liquid curves with solid-solid phase separation at bottom; b – shift of original (solid) phase boundaries to nonequilibrium (dashed) ones due to the effect of ultrafast cooling (cf. Table 1) exhibiting the consequences of preparation technology; c – possible change of the structure of phase boundaries when accounting chemical effect of strong interactions (cf. Table 2) between two components *A* and *B* to exhibit eutectic and peritectic points and incongruently melting compound *C*. It results from the system nonideality; d – inclusion of metastable phase boundaries (dashed lines) by extrapolation of equilibrium (solid) lines. It shows all possible stable and metastable states available at the system to occur as combined effect of system nonideality and experimental conditions of its treatment; e – possible experimental result while studying such a system (d) by thermal analysis upon heating. By fitting hypothetical experimental points (dots) the lines can assume a form of two separated, eutectic-type diagrams of the *A* component with *B* superposed to that of *A* with *C*. It is worth noting that the both experimentally detected horizontal lines must not necessarily represent stable phase boundary being often a source of false interpretation. Whatmore any of metastable boundary lines may appear as a potential source of an effect detectable by a given thermoanalytical technique in a more or less pronounced (or negligible) form depending on the sample history

References

1 J. Šesták, Thermophysical Properties of Solids; Their Measurement and Theoretical Thermal Analysis, Elsevier, Amsterdam 1984.

2 M. Nevřiva and J. Šesták, Thermodynamic Approach to Study Solid-Liquid Phase Equilibria in Uninvestigated Oxide Systems; in Thermal Analysis (Z. D. Živkovic, ed.), Collection of Papers of Technical University, Bor 1984 (Yugoslavia), p. 3.

3 L. H. Bennet, T. B. Massalski and B. C. Giassen (eds), Alloy Phase Diagrams, North Holland, Amsterdam 1983.

4 Moffat et al. (eds), The Structure and Properties of Materials, Vol. I., J. Wiley and Sons Inc., New York 1967.

5 J. Šesták, Z. Strnad and A. Tříska (eds), Modern Crystalline and Non-crystalline Materials and Their Technologies, Academia, Prague 1988; Elsevier, Amsterdam 1988 (in print).

6 T. A. Cherepanova, J. Crystal Growth, 52 (1981) 319.

7 Z. Chvoj, Cryst. Res. Technol., 21 (1986) 1003.

8 Z. Chvoj, Czech. J. Phys., 1987 (in print).

9 M. Nevřiva and J. Šesták, Thermochim. Acta 92 (1985) 623.

10 Z. Chvoj, A. Tříska and J. Šesták, Kinetic Phase Diagrams (in course of preparation) Academia, Prague 1989; Elsevier, Amsterdam 1989.

Zusammenfassung — Es wird eine theoretische Untersuchung der Bildung von Stoffen mit metastabilen Mikrostrukturen unter nichtidealen Bedingungen weitab vom Gleichgewicht dargelegt.

Резюме — Представлен теоретический анализ образования веществ с метастабильными микроструктурами в неидеальных и сильно неравновесных условиях.