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On systematics and nomenclature of crystallization reactions in solid alloys*

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Crystallization reactions which start in an amorphous or crystalline phase are compared. The following three elementary mechanisms are distinguished: (a) structural transformation of the total volume: massive transformation, polymorphous crystallization; (b) partial preservation of the matrix and local changes in composition: precipitation, primary crystallization; (c) combinations of transformation and decomposition: eutectic and eutectoid reactions. Necessary and sufficient conditions for the occurrence of these reactions are discussed with special concern for metastable equilibria and kinetics which control crystallization of metallic glasses.

Nomenclature

b (m),	atomic distance
D_a (m^2 sec^{-1}),	diffusion coefficient
F_a (J mol^{-1}),	free energy of the amorphous phase
F_α (J mol^{-1}),	free energy of a crystalline phase
$\Delta F_{a\alpha}$ (J mol^{-1}),	$\Delta F_{a\alpha} = F_a - F_\alpha$
RT (J mol^{-1}),	thermal energy
S (m),	diffusion path/lamellar spacing
T (K),	temperature
T_g (K),	glass transition temperature
T_m (K),	melting temperature
$\dot{T}$ (K sec^{-1}),	average cooling rate
$\bar{V}'$ (m^3),	average atomic volume in metastable equilibrium
$\bar{V}''$ (m^3),	average atomic volume in frozen-in state
$\bar{V}_f$ (m^3),	average free volume per atom
$\dot{X}_1$ (m sec^{-1}),	velocity of the front of massive reaction
$\dot{X}_3$ (m sec^{-1}),	velocity of the front of eutectic reaction
l, α, β, γ,	phases in stable equilibrium
l′, a′, α', β',	phases in metastable equilibrium
a″, α'',	frozen-in phases
P,	precipitation reaction
T,	transformation reaction
C,	combined reaction, eutectic or eutectoid

1. Metastable and stable equilibria, and frozen-in structures

Recent advent of interest in metallic glasses has provided us with a wealth of observations on crystallization reactions. These reactions start in the amorphous structure which is partially or completely transformed into one or more crystalline phases [1–3]. These phenomena are supplementary to earlier observations on crystallization from liquids [4], as well as the formation of new crystals in an already crystalline matrix [5, 6]. In this discussion crystallization from the liquid will be excluded but aspects of crystallization from amorphous and crystalline solids will be compared, i.e. atomic transport takes place by diffusion or homogeneous shear but not by convection.

A metallic glass always originates if a liquid, l, is cooled below the melting temperature, T_m, and no crystallization has taken place. This structure becomes metastable (l′ → a′) and relaxes corresponding to the metastable thermodynamic equilibrium until it will freeze-in at a temperature range of $\frac{1}{2}T_m < T_g < \frac{2}{3}T_m$ (Fig. 1). A particular structure of the metastable liquid stays constant during further cooling to $T < T_g$. T_g, and consequently the structure of the glass (a″), will vary as a func-

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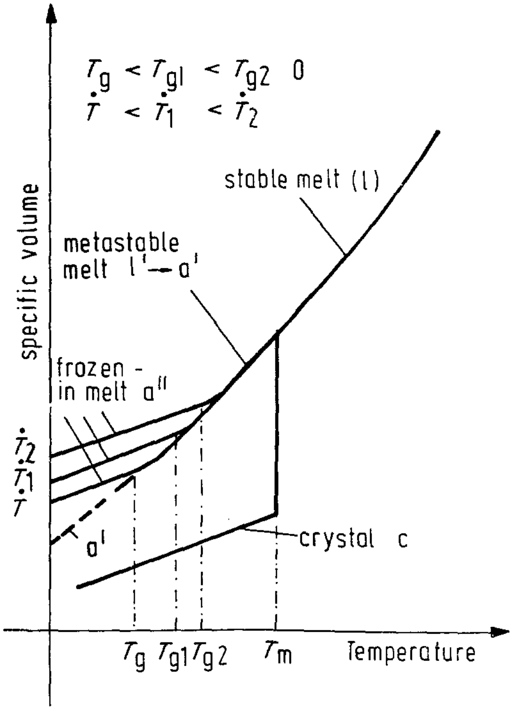


Figure 1 A schematic illustration of the specific volume–temperature diagram showing the structures which form during cooling of a liquid, l, at different rates, $\dot{T}$.

tion of the rate of cooling, depending on how much time was left for relaxation towards the equilibrium structure. In all our consequent discussions stable (l), metastable (l′→a′), and frozen-in structures (a″) will have to be distinguished. A frozen-in structure can contain a surplus of defects as well as of solutes atoms. If a crystalline solid solution is quenched across a solubility line, it will always contain not only atoms but also vacancies in supersaturation. Similar but less well defined are the defects which appear as the free volume, $\bar{V}_f$, of a frozen-in liquid [7]:

$$\bar{V}_f(\dot{T}) = \bar{V}''(T, \dot{T}) - \bar{V}'(T). \qquad (1)$$

Owing to the energy of the defects, the free energy of the frozen-in state is higher than that of the metastable structure. There will always be a tendency for relaxation and consequent ageing of a glass before it transforms into the stable crystalline state.

$$a'' \rightarrow a' \qquad (2)$$

The term metallic glass should be used for a material which has been obtained by freezing-in an undercooled liquid. Macroscopic properties like the coefficient of thermal expansion or specific heat behave in this temperature range as during a second-order phase transformation. Freezing-in during cooling and re-approach to the metastable equilibrium is therefore sometimes confused with a second-order phase transformation.

The metallic glasses are a subset of amorphous metals. The latter can be produced either by destruction of a crystal (by radiation, shock waves, plastic deformation) or by the condensation of individual atoms (by vapour deposition, electrolytic deposition). Metallic glasses represent a special case in between these two extremes.

2. Necessary and sufficient conditions for the occurrence of transformation, precipitation, and combined reactions

In case of transformation the original structure disappears completely and is replaced by a new one (Fig. 2).

$$a'' \rightarrow \alpha \qquad (3a)$$

$$\alpha'' \rightarrow \beta \qquad (3b)$$

a″ is a metallic glass and α″ is a supersaturated solid solution. Both may be obtained by quenching from a temperature at which they are thermodynamically stable. In solid solutions a″ or α″, these reactions can pass a transitional two-phase stage:

$$a'' \rightarrow a' + \alpha' \rightarrow \alpha \qquad (3c)$$

$$\alpha'' \rightarrow \alpha' + \beta' \rightarrow \beta. \qquad (3d)$$

For its starting period the precipitation reaction is similar to transformation. However, a portion of the original structure is always preserved and a local change in chemical composition is required for precipitation:

$$a'' \rightarrow a' + \alpha' \qquad (4a)$$

$$\alpha'' \rightarrow \alpha' + \beta' \rightarrow \alpha + \beta. \qquad (4b)$$

Included in Equation 4b is the case when a metastable transitional condition is passed on the way to full equilibrium (Fig. 2). There exist reactions in which structure and composition change simultaneously.

$$a'' \rightarrow \alpha + \beta \qquad (5a)$$

$$\alpha'' \rightarrow \beta + \gamma \qquad (5b)$$

The necessary conditions for the occurrence of the three types of crystallization reactions can be derived from the relative thermodynamic stability of the particular phases by using free energy-composition (*F*, *x*) diagrams. Fig. 3 represents an

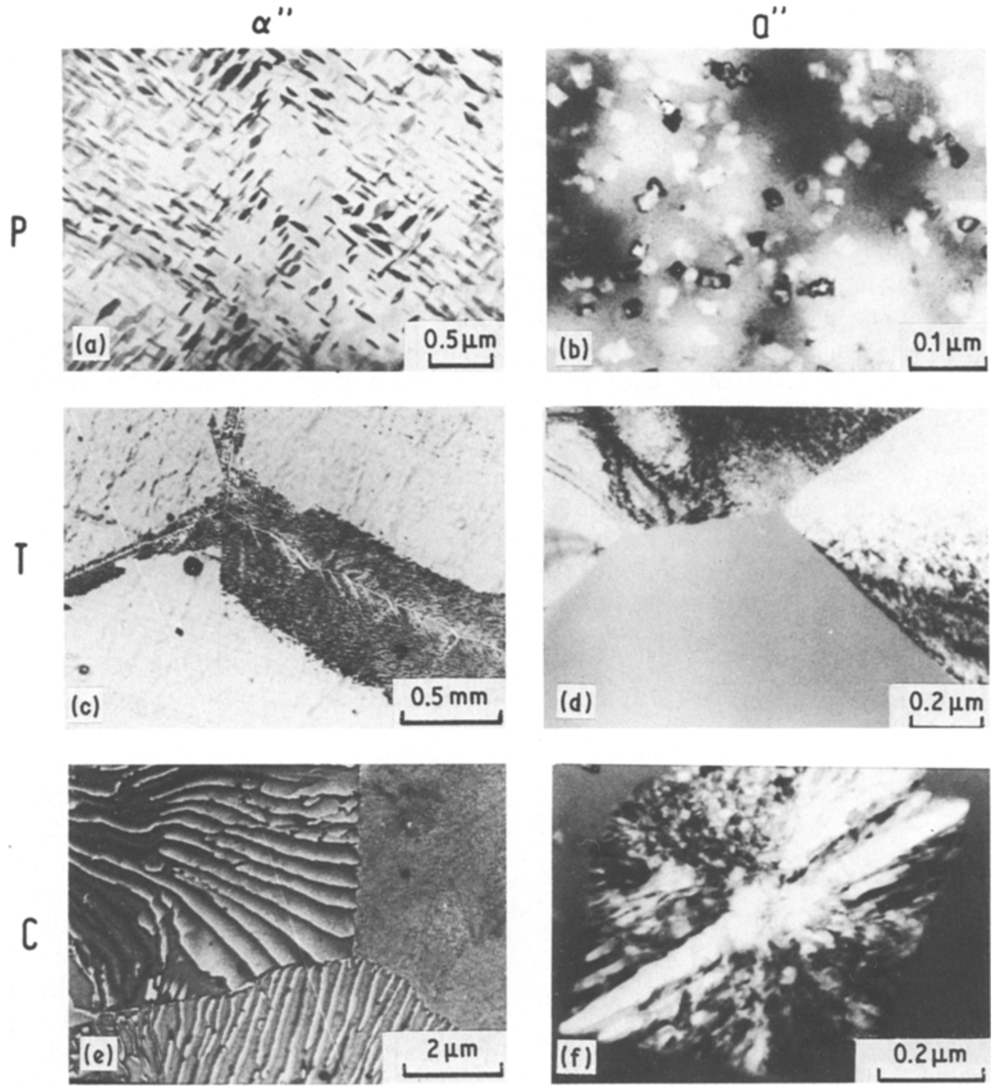


Figure 2 Microscopic investigations of crystallization reactions from crystalline α'' and non-crystalline a'' solids (see Table I): (a) precipitation of θ'-Al_2Cu from Al + 4 wt% Cu, 100 h, 300° C (TEM); (b) precipitation of α-Fe(Mo) from an $Fe_{75}Mo_9C_{16}$ glass, 10 min, 480° C; (c) massive transformation to α-CuZn from β-CuZn in copper + 39 wt% Zn + 1 wt% Sn (LM); (d) massive or polymorphous crystallization of hexagonal ϵ-phase from an $Fe_{81}C_{19}$ glass during splat cooling (TEM); (e) eutectoid transformation of a γ-Fe in iron + 0.8 wt% C at 690° C (replica, TEM); (f) eutectic crystallization of α-(Fe, Cr) and $(Fe, Cr)_3C$ from a $Fe_{49}Cr_{31}C_{20}$ glass (TEM).

example showing the differences $\Delta F_{a\alpha} = F_a - F_\alpha$ between an amorphous and several crystalline phases. Clearly defined are the compositional ranges in which the three types of reaction can occur. However, they occasionally overlap and they will either lead to metastable or to stable equilibria. If a metastable equilibrium is approached by the first part of the reaction, a secondary stage must follow. Equation 4a is, for example, followed by crystallization of a':

$$a'' \rightarrow a' + \alpha' \rightarrow \beta + \alpha. \qquad (6)$$

As the phase-diagram maps the equilibrium compositions as a function of temperature, information about the metastable equilibria can be obtained by extrapolation of equilibrium functions (Fig. 4). This (T, x)-diagram can be used as a map which shows the temperature–composition areas in which the necessary conditions for the occurrence of certain stable or metastable equilibria are fulfilled. The question arises: what is a sufficient condition for the occurrence of a metastable instead of a stable structure? In addition to the existence of a metastable equilibrium the reaction towards it must proceed faster than that towards the more stable one.

Without an understanding of the details of reaction mechanisms, no prediction can be made on which reaction is actually found in the compositional ranges indicated as A-1, 1-2, . . . , etc., in Fig. 6. The reaction rate is controlled by both nucleation and growth of one (Equations 3 and 4) or two (Equation 5) new phases (Fig. 5). The metastable equilibria (Figs. 3 and 6) resemble situations where either the nucleation of α or β from the glass a″ is improbable. Then the primary reaction is of the type indicated in Equation 4 instead of Equation 5. There are other situations for which nucleation occurs at about the same rate. However, the velocities of the reaction fronts are quite different. An example is the competition between a transformation reaction and the combined reaction (Fig. 6). The driving force for the combined reaction is always the largest one (Fig. 3). However, it requires long-range diffusion ($S \gg b$), while a transformation reaction can proceed by single atomic hops:

$$\dot{X}_1 = \frac{2D_a}{b}\,\frac{\Delta F_{a\alpha}}{RT} \qquad (7a)$$

$$\dot{X}_3 = \frac{4D_a}{S}\,\frac{\Delta F_{a\alpha+\beta}}{RT} \qquad (7b)$$

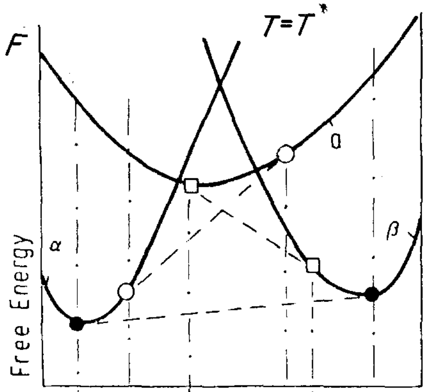
The sufficient conditions for a definition of the composition at which Reaction 1 is replaced by Reaction 3 (for the pre-requisites made on nucleation) are determined by the ratio of the two reaction velocities (Figs. 3 and 6):

$$\begin{array}{ll} \dot{X}_1 > \dot{X}_3 & \text{transformation,} \\ \dot{X}_1 = \dot{X}_3 & \text{transition,} \\ \dot{X}_1 < \dot{X}_3 & \text{combined reaction.} \end{array} \qquad (8)$$

If a transformation reaction has taken place from an amorphous phase, the reaction product can be crystalline but metastable (a″ → α′). Therefore, a secondary reaction is required (Equations 3b and 4b) to obtain the complete phase equilibrium.

In addition to the entropy of mixing the shape of free-energy functions (Figs 3 and 6) is determined by the atomic size ratios and the electronic interactions between the atoms of an alloy. For the prediction of the glass-forming ability of an alloy these functions alone provide neither information of necessary nor of sufficient requirements, as this is sometimes claimed. For this purpose it is always necessary to include properties

Figure 3 Free energy–chemical composition (F, x) diagram for a temperature T^*. One or two crystalline phases (α, β) can form from an amorphous matrix, a.



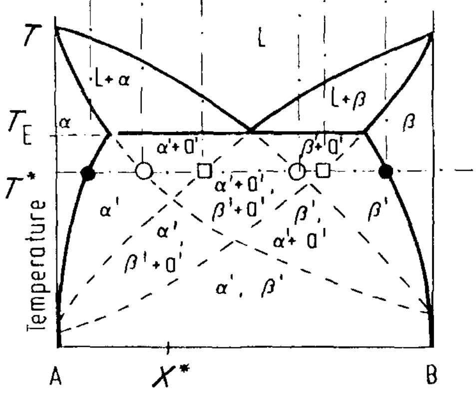


Figure 4 A plot of temperature against chemical composition (T, x) of a eutectic alloy system with limited mutual solubility in the α-, and β-phases. The (l + α)- and (l + β)-equilibria have been extrapolated to temperatures $T < T_E$.

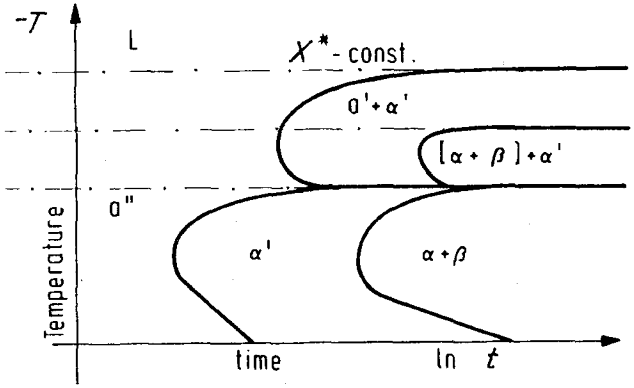


Figure 5 Temperature–time of crystallization diagram for an alloy X^* (indicated in Fig. 4).

TABLE I Systematic survey of crystallization reactions which start from a metallic glass a'' or from a supersaturated crystalline phase α'' (cf. Fig. 2)

Diffusion conditions	Starting phase	Precipitation	Transformation	Combined reactions
Long-range diffusion, $S \gg b$	a''	$a'' \rightarrow a' + \alpha'$ Precipitation from a glass or primary crystallization	$a'' \rightarrow a' + \alpha' \rightarrow \alpha$ crystallization with segregation	$a'' \rightarrow \alpha + \beta$ eutectic crystallization
	α''	$\alpha'' \rightarrow \alpha + \beta$ Precipitation from a crystal	$\alpha'' \rightarrow \alpha' + \beta' \rightarrow \beta$ transformation with segregation	$\alpha'' \rightarrow \beta + \gamma$ eutectoid transformation
Short-range diffusion, $S \approx b$	a''		$a'' \rightarrow \alpha$ massive crystallization or polymorphous crystallization	
	α''		$\alpha'' \rightarrow \beta$ massive transformation	$\alpha'' \rightarrow \beta'_M + \gamma'$ bainitic transformation
Diffusionless	α''		$\alpha'' \rightarrow \beta_M$ martensitic transformation	

of the crystalline phases and their kinetics of formation in the considerations.

3. Systematics of the crystallization reactions

Table I represents all the reactions which can start from an amorphous a'' and from a crystalline structure α''. Precipitation (or decomposition) in the amorphous phase is not included because crystals are not yet formed:

$$a'' \rightarrow a'_1 + a'_2. \qquad (9a)$$

Also excluded are reactions in which only free volume (Equation 1) or lattice defects are healing out such as:

$$a'' \rightarrow a'. \qquad (9b)$$

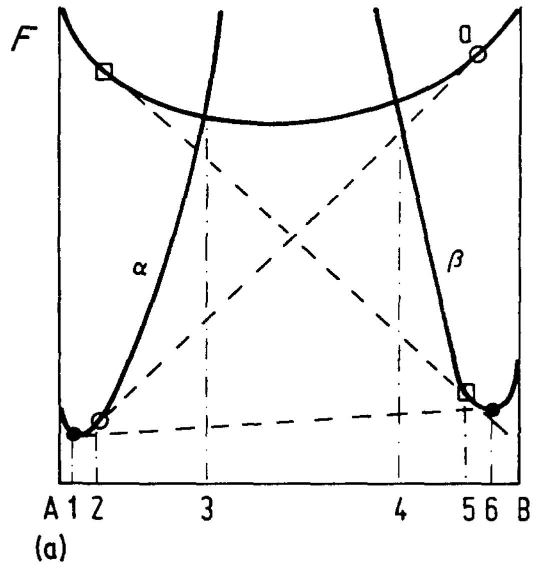
All crystallization reactions can be divided into three groups depending on whether their mechanism requires:

(1) long-range diffusion $S \gg b$;
(2) only individual atomic jumps $S = b$;
(3) no diffusion.

A particular transformation reaction in crystals (Equation 3b) is known as massive transformation (Fig. 2). For the corresponding reaction from the amorphous structure the term polymorphous crystallization is sometimes used. This is not quite plausible because polymorphism commonly applies to a situation in which a material can crystallize into two or more structures. In analogy to massive transformation, massive crystallization could possibly be applied to describe this type of reaction. For the process of precipitation of crystals from a glass, the term primary crystallization is used in analogy to crystallization from a liquid. Eutectic crystallization and eutectoid transformation are well established for the combined reactions. Only the bainitic reaction does not fit completely into this scheme. It is a combined reaction, namely a combination of martensitic transformation, followed by precipitation or segregation to lattice defects. The diffusion paths are never very large if, for example, segregation at stacking faults or precipitation of very finely dispersed particles occurs.

4. Conclusion

Crystallization reactions in solids can start from metastable equilibria and from frozen-in structures. A metallic glass is an amorphous metal which has been obtained by freezing-in a metastable liquid. Transformation, precipitation and combined reactions are found in amorphous or crystalline structures depending on whether the structure, or composition, or both, change during the reaction. A necessary condition for their occurrence is the existence of a driving force, i.e. a positive difference between a free energy of starting structure and final structure. A prediction of what type of reaction will actually take place and whether a metastable equilibrium is formed is possible only if details of reaction kinetics (nucleation, growth mechanism) are considered. The sufficient conditions are provided by the principle that the reaction will be selected which takes place at the highest rate. A systematic



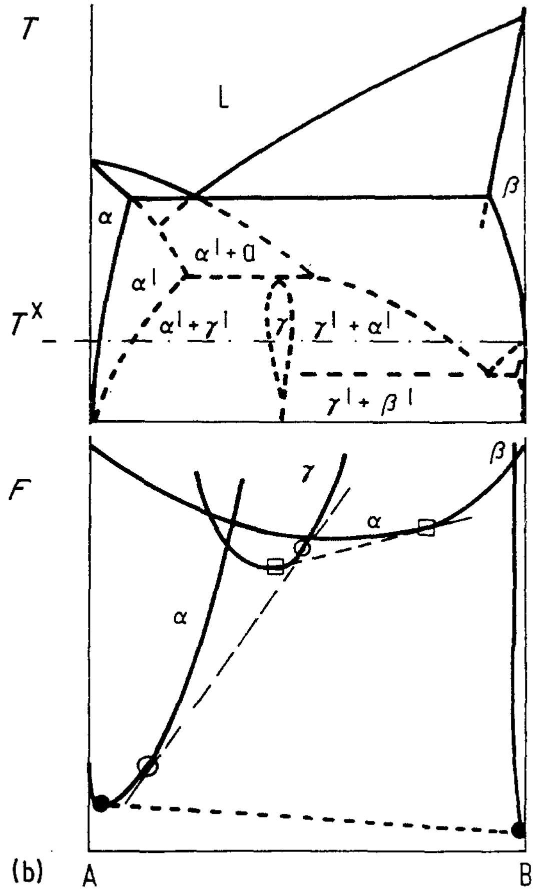


Figure 6 Relations between the (*F*, *x*) diagram to structures of phases which form during crystallization reactions. (a) (*F*, *x*) diagram (see Fig. 3) showing stable and metastable heterogeneous equilibria. Table II gives compositional ranges for which the necessary conditions of the occurrence of transformation (T), precipitation (P), or eutectic crystallization (C) from an amorphous phase a'' are fulfilled. (b) (*F*, *x*) and (*T*, *x*) diagrams showing the necessary conditions for the formation of a new metastable phase by crystallization from a glass.

TABLE II Primary reactions from a'' for which the necessary condition is fulfilled for a driving force to exist

Reaction	Composition						
	A–1	1–2	2–3	3–4	4–5	5–6	6–B
T	α	α'	α'	–	β'	β'	β
P	–	–	$\alpha' + a'$	–	$\beta' + a'$	–	–
C	–	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	–

survey is based on a comparison of reactions which start from supersaturated crystals and amorphous alloys.

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