

## On the description of solid state amorphizing reactions

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**Abstract.** Growth of the metastable amorphous phase instead of stable crystalline phases in the process of chemical diffusion is explained in the framework of the theory of diffusional phase competition. The growing amorphous phase suppresses nucleation as well as the growth of crystalline phases for some time. The suppression time and the corresponding width of the amorphous layer are evaluated. The reasons for the appearance of the initial amorphous layer are discussed.

Amorphous metallic alloys have been produced recently by solid state reaction [1-6]. The various aspects of such transformations can be naturally explained on the basis of the concept of diffusional phase competition which was developed earlier by one of us and a co-worker [7-9]. The main point of this concept is the simultaneous analysis of diffusional interactions and nucleation of intermediate phases in the field of concentration gradients. Amorphizing reactions are correctly explained in this case and the nucleation of the metastable amorphous phase (AP) is elucidated.

Let us review the main positions of the theory [7-9]. Phase growth in the diffusion zone begins by the nucleation of intermediate phases as a result of heterophase fluctuations. A nucleus is thermodynamically stable if its radius exceeds a critical value (if the gain in the free energy of the volume begins to exceed the loss in surface energy). The fundamental difference from phase formation by alloy cooling is as follows: the phase nuclei are formed in the field of chemical potential gradients and therefore immediately begin to interact diffusionally with parent phases and/or with the nuclei of other intermediate phases. This diffusional interaction is described mathematically by a system of balance equations for the fluxes on the moving interphase boundaries. As a result the growth velocity of some critical nuclei appears to be negative so that their size starts to decrease, transforming into embryos with a subcritical size. Such embryos are thermodynamically unstable and must dissociate. This means that certain intermediate phases from the phase diagram of the system can be absent in the diffusion zone for some time (which can be rather a long time). To be more precise, such suppressed phases are virtually present, in the form of forming, decreasing and dissociating nuclei. The corresponding criteria of phase growth and suppression were obtained.

For the simple case of two intermediate phases for mutually insoluble components the main defining factor is the value of the ratio

$$r = (D_1 \Delta C_1 / D_2 \Delta C_2) l_2 / l_1$$

where the diffusivities are

$$D_i \Delta C_i = \int_{(\Delta C)} D(c) dC$$

$\Delta C_i$  is the concentration range of the  $i$ th phase and  $l_i$  is the critical nucleus size of the  $i$ th phase. If  $r < C_1/C_2$ , in the initial period only phase 2 (the 'vampire' phase) grows, suppressing the nuclei of phase 1. If  $C_1/C_2 < r < (1 - C_1)/(1 - C_2)$ , both phases grow from the very beginning. If  $r < (1 - C_1)/(1 - C_2)$ , only phase 1 grows initially, suppressing phase 2.

Phase suppression cannot continue infinitely. As the suppressing ('vampire') phases grow, the concentration gradients and corresponding fluxes along the phase layers decrease, their growth velocity decreases and their 'competition ability' decreases also.

For every suppressed phase the moment comes (if the diffusion couple is sufficiently long) when the growth velocity of its critical nuclei becomes positive and they start to grow. The time of diffusional suppression of the phase nuclei was called an incubation period. Evidently, it is only the 'diffusional' part of the full incubation period. The process mentioned above was called diffusional phase competition.

We shall see that the concept of diffusional competition enables us to explain some peculiarities of diffusional amorphization if one assumes that the nuclei of the metastable AP are formed in the diffusion zone.

Let us consider four typical situations.

(i) The amorphous layer forms and grows in the process of low-temperature annealing of polycrystalline pairs (Au-La, Fe-Zr, Co-Zr, Cr-Ti, etc [4-6]).

(ii) If a nickel film is deposited on a Zr single crystal, an amorphous layer does not form.

(iii) If such a pair consisting of Ni and a Zr single crystal is irradiated beforehand by a high-energy ion beam, the amorphous layer forms and grows inside the single crystal.

(iv) If one deposits a thin film of polycrystalline Zr on the Zr single crystal and then a layer of Ni, an AP forms first on the base of the polycrystalline layer and then grows inside the single crystal [6].

During the growth of the amorphous layer the intermetallic compounds with concentration ranges neighbouring or overlapping with that of the metastable AP are absent for rather a long time. Let us discuss this point in detail.

For intermediate phase formation in the process of chemical diffusion the three following conditions should be fulfilled.

(i) With respect to the composition preparation, the region with concentrations in the interval  $(C, C + \Delta C)$  must have a width not less than the critical size  $l_{cr}$  for this phase. The real situation is much more complicated and corresponds to the problem of nucleation in the field of the concentration gradient. This problem was solved in [9-11]. In the simplified form the result can be presented as follows: nucleation becomes possible only after some time, when the gradient has decreased and the diffusion zone has become wide enough:

$$L > l_{cr}/\Delta C.$$

(ii) After the preliminary stage, nuclei of the new phase have to form by a process of fast polymorphous transformation without composition changes. In the process of

polymorphous transformation, nuclei grow preferentially in the transverse directions and form the initial layer.

(iii) The initial layer consisting of critical nuclei forms in the field of chemical potential gradients and, therefore, enters the diffusional phase competition. Let us begin from this stage.

Let the nucleus of intermetallic compound 1 appear between the amorphous layer and the parent material B ( $C = 1$ ). Let us consider the case when phase 1 is in the state of metastable quasi-equilibrium with the AP and the dilute solution of A in B (figure 1). The motion of the interphase boundaries AP-1 (coordinate,  $X_L$ ) and  $i$ -B (coordinate,  $X_R$ ) is determined by the balance equations

$$\begin{aligned}(C_i - C'') dX_L/dt &= (D_{AP} \Delta C_{AP})/\Delta X_{AP} - (D_i \Delta C_i)/\Delta X_i \\ (1 - C_i - \Delta C_i) dX_R/dt &= (D_i \Delta C_i)/\Delta X_i \\ \Delta X_i &= X_R - X_L \quad \Delta C_{AP} = C'' - C'.\end{aligned}\quad (1)$$

From equations (1) follows the growth rate of the  $i$ th phase:

$$\begin{aligned}d(\Delta X_i)/dt &= (1 - C_i)^{-1} \\ &\times [(1 - C'')/(1 - C')(D_i \Delta C_i)/\Delta X_i - (D_{AP} \Delta C_{AP})/\Delta X_{AP}].\end{aligned}\quad (2)$$

An intermetallic phase can grow from the nucleus only under the condition  $[d(\Delta X_i)/dt]_i > 0$ . According to equation (2), this is possible only if

$$\Delta X_{AP} > \Delta X_{AP}^m = [(C_i - C'')/(1 - C'')][(D_{AP} \Delta C_{AP})/(D_i \Delta C_i)]l_i. \quad (3)$$

If  $\Delta X_{AP} < \Delta X_{AP}^m$ , the forming nuclei would be dissolved by the fast-growing AP. In this period ( $t < \tau_3$ ), only the AP will grow, according to the parabolic law

$$\Delta X_{AP} = \{[2(1 - \Delta C_{AP})(D_{AP} \Delta C_{AP})]t/[C'(1 - C'')]\}^{1/2} \quad t < \tau_3. \quad (4)$$

Equations (2) and (3) lead to the expression for the diffusional incubation period:

$$\tau_3 = [C'(C_i - C'')^2/2(1 - \Delta C_{AP})(1 - C'')][(D_{AP} \Delta C_{AP})/(D_i \Delta C_i)^2]l_i^2. \quad (5)$$

As was shown, for example, in [12], as a crude approximation we can take  $D_i \Delta C_i \sim C_i D_A + (1 - C_i) D_B$ . Taking this evaluation into account, let us suggest Bugakov's rule for a compound with a congruent melting point  $T_m$ :

$$D_i \Delta C_i \sim 1 \text{ (cm}^2 \text{ s}^{-1}\text{)} \exp(-17.5T_m/T).$$

From the data for the growth rate in the system Ni-Zr [6], one can evaluate  $D_{AP} \Delta C_{AP}$  according to (4): approximately  $4 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ . Evaluation of  $D_i \Delta C_i$  from a Bugakov-like relation gives a value of about  $7 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$ . Then, if one takes  $l_i = 10^{-9} \text{ m}$ , the value  $\Delta X_{AP}^m$  (when  $\Delta X_{AP} < \Delta X_{AP}^m$ , the  $i$ th

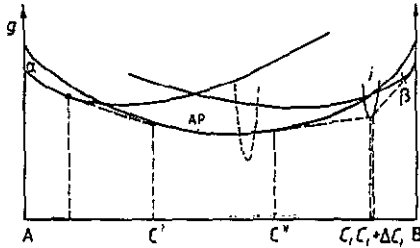


Figure 1. Gibbs' free-energy dependence on concentration for the AP, the intermetallic phase and the initial phase.

phase is suppressed), is determined from (3) and gives a value of about  $10^{-6}$  m. (In fact, this compound appeared when  $\Delta X_{AP} \approx 0.15 \times 10^{-6}$  m.)

Thus, a long absence of an intermetallic phase between the amorphous layer and one of the parent components is explained well by the diffusional suppression of intermetallic nuclei by the fast-growing AP.

The second important question is why the expected stable compounds do not appear between the parent components instead, or at least on the base of the amorphous phase, which is metastable and therefore less favourable in the thermodynamic sense. If an AP had time to be created, the equilibrium intermetallic compounds in the same concentration range have to form on the basis of this phase. In this case three additional obstacles appear.

(a) Nucleation is homogeneous (the AP has no inner boundaries nor other planar and linear defects).

(b) The critical size  $4\sigma v/\Delta g$  is substantially higher owing to a reduced thermodynamic force  $\Delta g$  of transformation which is now taken relative to the metastable (and not parent) phase.

(c) Nucleation is impossible until the AP attains a width

$$L_c \approx (\Delta C_{AP}/\Delta C_i)l_{cr}.$$

If one takes  $\sigma = 10 \text{ J m}^{-2}$ ,  $v = 10^{-29} \text{ m}^3$ ,  $\Delta g = 10^{-19} \text{ J}$ ,  $\Delta C_i = 0.01$  and  $\Delta C_{AP} = 0.5$ , then

$$l_{cr} \approx 4 \times 10^{-9} \text{ m} \quad L_c \approx 2 \times 10^{-7} \text{ m}.$$

The last question remains: how can nuclei and the initial layer of metastable AP form in the system? The experiments mentioned above show that the AP nucleation is connected with the polycrystalline structure of parent materials or with the effect of irradiation. It is well known [13] that for the nucleation on a grain boundary (GB) the free-energy barrier vanishes under the condition  $\sigma_{\alpha\alpha} > 2\sigma_{\alpha-AP}$  where  $\sigma_{\alpha\alpha}$  is a surface GB energy,  $\sigma_{\alpha-AP}$  is an interfacial energy per unit surface. One can suppose the existence in a polycrystalline material of amorphous-like boundaries (with a high  $\sigma_{\alpha\alpha}$ -value) which decrease the nucleation barrier. An even more probable centre for nucleation ought to be a GB junction. It was accepted in [14, 15] that GBs may act as nucleation centres in the formation of amorphous phases. Schröder *et al* [16] have already indicated the importance of the GB triple junctions.

Our equations and evaluations do not use the relation  $D_A \gg D_B$  as a necessary condition for the growth of an amorphous layer. We need only  $D_{AP} \Delta C_{AP} \gg$

$D_i$ ;  $\Delta C_i$ . Yet the fast penetration of one of the species through the GBs towards the future amorphous nuclei should promote the amorphizing reaction.

The idea of application of the competition theory to SSARS has been presented previously [17, 18]. A similar, but more phenomenological approach was suggested in [19]. (However, the 'fate' of the critical nuclei and diffusional suppression was not considered in detail nor was the problem of nucleation in the concentration gradient.)

Yet, for both approaches, the reason for rapid AP nucleation was not clear. This problem is solved if one considers GB junctions as the places of segregation followed by nucleation of the AP. A similar picture of the AP phase nucleation was presented in [20] (but the reasons for the suppression of stable phases were not considered there).

We can draw the following conclusions.

(i) Growth of the metastable AP in the diffusion zone in the process of chemical diffusion can be described with the help of the diffusional competition theory for stable phases. Thus, the theory of diffusional competition can be extrapolated to metastable phases.

(ii) Such a description is possible if the nucleation of the AP is made easier and AP nuclei exist in the system at the very beginning. Then the AP grows rapidly and suppresses the nucleation and growth of the stable crystalline phases for some time.

(iii) The nucleation of the AP can be promoted by the presence of some amorphous-like GB junctions and/or regions of GB intersections. In the case of single-crystal Zr, nuclei are provided by irradiation.

(iv) Thus, all known experimental situations are described in the framework of this approach. Experimental verification of the amorphous-like structure of the GB junctions is, however, needed.

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