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Crystallization kinetics

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Avrami's treatment of nucleation and growth kinetics considers that active nucleation sites are *randomly* distributed throughout the volume and that grains may *impinge* upon grains grown from other sites, causing growth to cease on the common interface. This treatment resulted in the well-known Avrami equation. As a result of the reassessment of these basic assumptions, an integral equation is proposed for the time-dependence evaluation of the transformed phase volume fraction in crystallization processes, instead of the Avrami equation. The proposed model fits very well the whole range of experimental data for $NiZr_2$ and $Te_{92}Pb_8$ amorphous to crystalline transformation.

In classical kinetic theory of first-order transformations,[1] nucleation of the product phase starts with the formation, at a certain temperature, of small unstable *embryo* clusters. Some embryos shrink, while others eventually grow to reach a critical size, beyond which they have a higher probability to grow than to dissolve, and becomes then (stable) *nuclei*. After a nucleus has reached its critical size at a certain site within the volume, the size of which depends on both temperature T and time t, the transformation proceeds by growth of the product phase and production of *grains*. The number of grains in the transformed volume is equal to the number of *active* nucleation sites. The physical entities involve in the transformation kinetics are the nucleation rate per unit volume, $I(T,t)$, and the growth rate $G(T,t)$ of the product phase. $I(T,t)$ is a function of the activation energy for the molecular migration involved in the transformation and the critical free-energy barrier, which itself is a function of the latent heat of transformation and the parent-product surface energy. $G(T,t)$, the velocity of the parent-product interface, depends mainly on the amount of undercooling at the parent-product interface.[2]

The evolution of the transformed phase with time and temperature is described by the well-known and widely used kinetic "Avrami equation."[3] Among the physical and mathematical assumptions in Avrami's treatment, two are of special importance: (a) As time proceeds during growth, some grains grown from sites active at various times in the past, may *impinge* upon grains grown from other sites. In this case, growth ceases on the common interface, though it continues normally elsewhere.[4] (b) Active nucleation sites are *randomly* distributed throughout the volume.

Impingement of grains one upon another creates a geometrical problem, which Avrami solves by introducing an "*extended*" volume, defined as the total volume of the grains, had their growth not been impeded by impingement. This issue of impingement has to be dealt with for the prediction of the new phase evolution, as it affects the transformed volume fraction.

Assumption (b) needs clarification: What is the volume where nucleation sites are randomly distributed throughout? It is either the entire volume undergoing transformation V_{total} or the untransformed volume V^a only. In the first case, chosen by Avrami, the total number of nuclei formed during the time interval dz is the sum of the actual new nuclei $IV^\alpha dz$ and the additional "phantom nuclei" $IV^\beta dz$, nucleated in the already transformed volume V^β. In this case, the actual number of nucleation sites, and therefore the actual transformed fraction are overestimated.

The present paper suggests adopting the second case, where randomness is assumed to prevail in the untransformed, time-dependent volume only. This choice excludes the nonexistent, "phantom" nuclei.[5] The reassessment of the impingement and randomness issues leads to an alternative relationship to Avrami's equation for the transformed phase evolution with time and temperature.[6]

During the nucleation stage, any nucleus grown from embryos has reached after a time z (the nucleation time) its "critical" volume (volume of a sphere with a critical radius). At any time $t>z$ and temperature T, the volume $v^\beta(T,t)$ of an individual product phase grain has grown isotropically to become

$$v_z^\beta(T,t)=\left(\frac{4\pi}{3}\right)G^3(T,z)(t-z)^3 . \tag{1}$$

Within the untransformed volume $V^\alpha=1-V^\beta$ the number of new nuclei formed in the time interval z and $z+dz$ is $I(T,t)V^\alpha(T,t)dz$.

In either solid-state or liquid-to-solid transformations, mutual interference of grains growing from different nuclei causes growth to cease in regions with common interfaces, when the condition $V^b \ll V^a$ is not satisfied anymore. As stated in Ref. 1, the problem is primarily geometrical, and has been treated by Avrami[3] by introducing the concept of "*extended volume*" of the transformed material, V^β_{ext}, given by

$$V^\beta_{\text{ext}}(T,t)=\int_0^t v_z^\beta(T,t)N(T,z)dz . \tag{2}$$

Following the suggestion presented before, the concentration of actual grains at any time t is

$$N(T,t)=\int_0^t I(T,z)(V_{\text{total}}-V^\beta)dz . \tag{3}$$

$V^\beta_{\text{ext}}(T,t)$ is the total transformed volume if impingement

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of growing grains is neglected.

By introducing the value of v^β as defined by Eq. (1) and of $N(T,t)$ as defined by Eq. (3) in Eq. (2), one gets[7] (for spherical grains)

$$V^{\beta}_{\text{ext}}(T,t)=\left[\frac{4\pi}{3}\right]\int_0^t G^3(T,z)(t-z)^3 I(T,z)(V_{\text{total}}-V^{\beta})dz . \tag{4}$$

What is the relation between $V^{\beta}_{xt}(T,t)$ and $V^{\beta}(T,t)$? Avrami answers this question as follows [Ref. 3(b)]: Any increase during the time interval dt of the transformed volume dV^{β} is accompanied by an increase of the extended volume dV^{β}_{ext}. However, only a fraction $(1-V^{\beta}/V_{\text{total}})$ of this last increase, dV^{β}_{ext}, lies in the previously untransformed volume, and contributes to V^{β}. Therefore,

$$\frac{dV^{\beta}}{dV^{\beta}_{\text{ext}}}=1-\frac{V^{\beta}}{V_{\text{total}}}=1-\xi . \tag{5}$$

Using Eqs. (4) and (5), we finally get

$$\xi(T,t)=\left[\frac{4\pi}{3}\right]\int_0^t G^3(T,z)I(T,z)(t-z)^3[1-\xi(T,z)]^2 dz . \tag{6}$$

If $G(T,t)$ and $I(T,t)$ are constant, as may be assumed in some cases,[1] one gets

$$\xi(T,t)=\frac{4\pi}{3}G^3 I\int_0^t (t-z)^3[1-\xi(T,z)]^2 dz . \tag{7}$$

The crystallization kinetics are described by an integral equation. This equation should be used instead of the well known Avrami equation:

$$\ln[1-\xi(T,t)]=-\left[\frac{4\pi}{3}\right]\int_0^t G^3(T,z)I(T,z)(t-z)^3 dz . \tag{8}$$

If $G(T,t)$ and $I(T,t)$ are constant, the Avrami equation reduces to

$$\xi(T,t)=1-\exp\left[-\frac{\pi G^3 I t^4}{3}\right] . \tag{9}$$

To our knowledge, Eq. (6) has no analytical solution. $\xi(T,t)$ may, however, be evaluated numerically, using the finite-difference method.

Equation (7) has been used to fit reported experimental results for amorphous to crystalline isothermal transformations in the $NiZr_2$ (Ref. 8) and $Te_{92}Pb_8$ (Ref. 9) alloys. The numerical values for the product $G^3 I$ have been deduced from the best fit. The best-fit results are shown in Figs. 1 and 2, where $\xi(T,t)$ is also shown when the Avrami equation, Eq. (9) is used, with the same $G^3 I$ values, shown on the graphs.

As seen in the figures, there is practically no deviation of the fit to the experimental data when Eq. (7) is used. If the Avrami equation (9) is used, deviations occur for both alloys above ≈40% volume fraction. The reason for these systematic deviations are due to the overestimation of the number of operative nucleation sites, by omitting the factor $(V_{\text{total}}-V^{\beta})$ in Eq. (4). This leads to an increased, wrong, transformed phase evolution rate when the Avrami equation is used. The numerical values of $G^3 I$ resulting from the best fits with Eq. (7) do reflect the swiftness of the transformations: rapid crystallization in the case of $Te_{92}Pb_8$ and slower crystallization in the case of $NiZr_2$.

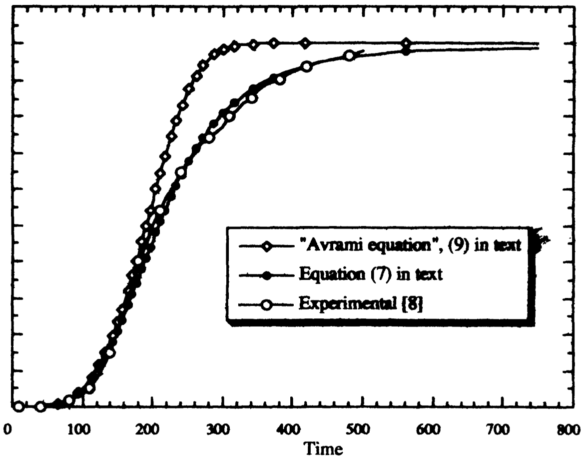

FIG. 1. Fraction crystallized vs time, $NiZr_2$, at 642 K.

Deviations from the fit for volume fractions above $x=0.50$ have been reported in numerous papers over the years, generally attributed to experimental artifacts. Reference 8, as an example, mentions a "larger than expected temperature gradient across the sample width." If the proposed integral equation is used for the data in Ref. 8, a single value for $G^3 I=5\times10^{-10}$ sec^{-4} fits the whole range of data up to $\xi=1$. Fitting the data to the (incorrect) Avrami's exponential equation with $G^3 I$ values either smaller and greater than 5×10^{-10} sec^{-4} does *not* afford any better fit.

We believe that Eq. (6) is applicable in kinetic analyses for solidification, crystal growth, polymorphic solid-state changes, discontinuous precipitation, eutectoid reactions,

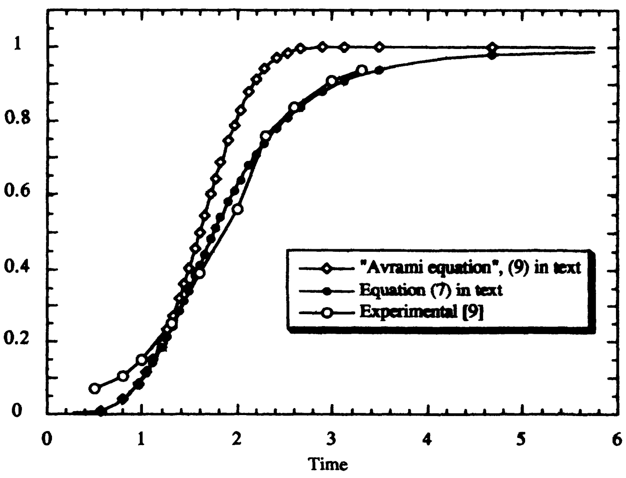

FIG. 2. Fraction crystallized vs time, $Te_{92}Pb_8$, at 319 K.

interface-controlled growth and diffusion-controlled growth in addition to crystallization from the amorphous state, in both isothermal and nonisothermal conditions.

This paper demonstrates that the Avrami's equation is a "simplification" of the real physical solution, resulting from the omission of the fact that the active nucleation takes place in the as yet untransformed part of the material, instead of the total volume system. This leads to an overestimation of the transformed volume, resulting in an incorrect evaluation of the temperature-dependent rate parameter, the nucleation rate and product-phase growth velocity, and of the power-law argument for the time, all of which serve to identify the physical nature of the transformation. It is still unclear how the kinetic parameters (activation energy and rate parameter) may be deduced from the general integral Eq. (6). This issue is currently being investigated.

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[1] J. W. Christian, *The Theory of Transformations in Metals and Alloys, Part I Equilibrium and General Kinetic Theory* (Pergamon, Oxford, 1975), Sec. 4.

[2] In general, the growth rate is anisotropic; however, in the present paper we assume, following Ref. 1, an isotropic growth rate G, so that the transformed regions are spherical.

[3] (a) M. Avrami, J. Chem. Phys. **7**, 1103 (1939); (b) **8**, 212 (1940).

[4] As remarked in Ref. 3, "this is usually true for crystalline growth," i.e., for solid-state phase transformations.

[5] Another approach could have been to subtract the "phantom nuclei" from the total number on nuclei to consider. This leads to the same final result.

[6] V. Erukhimovitch, Ph.D. thesis, University of Dnepropetrovsk, 1986.

[7] It should be stressed that the "extended" volume defined by Eq. (4) differs from the expression given by Christian (Ref. 1), as the latter includes "phantom" nuclei, i.e., is greater than the former one.

[8] S. Brauer, J. O. Strom-Olsen, M. Sutton, Y. S. Yang, A. Zaluska, G. B. Stephenson, and U. Koster, Phys. Rev. B **45**, 7704 (1992).

[9] F. Jiang, H. Wang, Y. Sun, and F. Gan, J. Non-Cryst. Solids **112**, 263 (1989).