Microalloying for the controllable delay of precipitate formation in metal alloys

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Abstract

A model is presented to predict the effectiveness of dilute solutes in delaying precipitate formation, with application to natural and artificial aging in metal alloys. Control of aging is achieved via the binding, at natural aging temperatures, and release, at artificial aging temperatures, of excess quenched vacancies by the solute atoms. The binding of vacancies to the solute atoms reduces the vacancy concentration in the bulk lattice, and thus reduces the rate of transport processes that control aging. To be useful, this strategy requires sufficiently strong, but not too strong, vacancy-solute binding, and sufficiently slow vacancy-solute diffusion, both quantified through application of the model. First-principles methods are used to compute the controlling materials properties (vacancy-solute binding energies and migration barrier) for a range of solutes in Al and Mg, and Pauli Electronegativity of the solute relative to the host metal is found useful for correlating properties. With the computed inputs, the model is applied to representative solutes (Ga, Sn, Pb) in Al that span weak to strong vacancy binding. Predictions of the model to Sn in Al are then shown to qualitatively agree with experiments, with quantitative agreement possible using a slightly stronger Sn-vacancy binding energy. The general model should be useful for identifying promising dilute solutes for control of precipitation/aging across many alloys in which quenched vacancies are used to control precipitation.

I. Introduction

Precipitation hardening is one of the most common methods of increasing the strength and hardness of metal alloys. Precipitates act to impede the motion of dislocations, the elementary units of plastic deformation in metals, where the size, shape, and density of precipitates determines the macroscopic yield strength¹⁻³. A given alloy system usually has a complex phase diagram including various metastable states. The precipitation process can thus be complex, as the system moves through a sequence of different phases, some desirable and others undesirable. Control of the precipitation process/path to achieve optimal performance has thus been a major field of study in metallurgy for decades³. In some systems, undesirable precipitation occurs even at ambient temperatures (natural aging), and subsequent treatment at elevated temperatures (artificial aging) is required for the dissolution of undesirable precipitates prior to the formation of desired precipitates. For instance, in Al-6xxx alloys for automotive applications, the goal is to form components in a pre-aged, low-strength state and then age them to optimal strength levels later in the production cycle. However, Al-6xxx alloys undergo natural aging, and thus strengthening, at room temperature, and this natural aging is undesirable for forming components and interferes with subsequent artificial aging. A general goal of

metallurgical processing is thus to control precipitation as fully as possible, so that the desired precipitation occurs when and where it is needed, with no other precipitation interfering with this process.

Precipitation/aging processes occur through a combination of solute diffusion and chemical reaction. The diffusion of a substitutional species i usually occurs via a vacancy-mediated process and so depends on the vacancy concentration c_V and the migration enthalpy barrier H_i^m ⁴⁻⁷, with a diffusion coefficient $D_i \sim c_V e^{-H_i^m/k_B T}$. Control of aging is thus possible, in principle, by control of the available vacancy concentration c_V . Quenching from elevated temperatures to low temperatures can lead to a supersaturation of vacancies, i.e. more vacancies than would exist in equilibrium at the low temperature, which can accelerate aging processes. However, the quenched vacancies needed to accelerate artificial aging may also accelerate undesirable natural aging. Controlling aging processes in alloys has thus presented challenges in the metallurgy field.

In this paper, we expand on a recent concept for controlling precipitation, with Al alloys as the primary initial application. The key concept is that of controlled binding and release of vacancies, i.e. modulation of the vacancy concentration in the metal lattice, via the introduction of a dilute concentration of an additional solute that binds vacancies. The process is envisioned as shown schematically in Figure 1, where we consider only the matrix material and the additional solutes, neglecting the solutes that will ultimately be responsible for precipitation. The material is held at a solutionizing temperature, T_S , which determines the vacancy population in the system. The material is then quenched. During the initial stages of quenching, vacancies move rapidly and are annihilated due to various processes, maintaining equilibrium concentrations at the current temperature. However, at some temperature, denoted by an effective solutionizing temperature T_S^{eff} , vacancy diffusion becomes sufficiently slow, and diffusion distances for annihilation sufficiently long, that the total number of vacancies in the material becomes constant, i.e. there is negligible annihilation during further cooling⁸. The number of vacancies in the bulk metal lattice at this stage is denoted $c_V(T_S^{eff})$. During further cooling, the existing vacancies repartition among the bulk lattice sites and the sites adjacent to the added solutes, since this requires only short-range vacancy motion. After quenching to the final (natural aging) temperature T_{na} (e.g. room temperature), those vacancies that are bound in vacancy-solute complexes (Figure 1b) are unavailable to participate in the diffusive processes of the precipitate-forming alloying elements. The concentration of vacancies in the lattice that can aid diffusion is reduced to some value $c_V(T_{na})$. Since diffusion is directly proportional to the vacancy concentration, if vacancy-mediated diffusion controls the kinetics of the precipitation processes, then natural aging is slowed by a factor $R(T_{na}) = c_V(T_S^{eff})/c_V(T_{na})$. Upon heating to the artificial aging temperature T_{aa} , the vacancies again repartition, with some vacancies released from the solutes and re-entering the bulk matrix (Figure 1c). Diffusion, and thus precipitation, processes are then slowed by a factor $R(T_{aa}) = c_V(T_S^{eff})/c_V(T_{aa})$. If the concentration of added solutes is sufficiently high, and if the binding of vacancies by these solutes is within some appropriate range, then one can achieve $R(T_{na}) \gg 1$ during natural aging but $R(T_{aa}) \sim 1$ during artificial aging, so that natural aging is strongly inhibited but artificial aging is only mildly modified. We have termed this concept to control precipitation as “diffusion on demand”, and it has recently been demonstrated for the case of dilute Sn additions to the Al-6061 Al-Mg-Si alloy⁹.

Here, we present the general thermodynamic model for the repartitioning of vacancies between bulk matrix and added solutes to compute $R(T)$ at any temperature T . Our analysis

makes several assumptions. First, we neglect vacancy annihilation below T_S^{eff} so that the total number of vacancies in the system remains constant at all lower temperatures. Models for annihilation have been developed and can be used to estimate T_S^{eff} as a function of microstructural features⁸. Second, we assume that the free vacancies in the matrix control the precipitation kinetics via the control of diffusion processes. **Third, we assume that the addition of the new solutes does not alter the chemistry or thermodynamics of the desired precipitation processes in the alloy; the concept here is to change only the kinetics of the precipitation processes of the base alloy. Thus, we consider the dilute limit of added solutes. The present analysis must thus be supplemented by thermodynamic analyses of the solubility of the added solute and of possible precipitate phases involving the added solute; these topics are not discussed here. Finally, we note that trapping of vacancies by the alloying elements is largely independent of the trapping by the dilute solutes, and is already included in the diffusion rates of the alloying elements in the base alloy.** The remainder of this paper is organized as follows. In Sec. II, we derive the thermodynamic model for the vacancy concentration in the lattice to obtain an expression for the retarding factor $R(T)=c_V(T_S^{eff})/c_V(T)$ for diffusion-controlled kinetic processes occurring at temperatures $T < T_S^{eff}$. In Sec. III, we assess the diffusion of vacancy-solute complexes to ensure that such diffusion does not undermine the thermodynamic retarding factor R . In Sec. IV, we present results of first-principles computations of the vacancy binding and migration energies relevant to the model. In Sec. V, we apply the model generally for several solutes in Al, and assess the role of single versus multiple vacancy binding, solute concentration, and other material parameters in controlling natural and artificial aging.

II. Thermodynamic Model

We consider the problem of a crystal lattice of $N_{latt} = N_m + N_S + N_V^{tot}$ sites containing N_m host metal atoms, N_S substitutional solutes, and N_V^{tot} vacancies in the system. We neglect the presence of other solutes that will be involved in precipitation. In all cases of interest, the number of vacancies and solutes is orders of magnitude smaller than N_m so that $N_{latt} \approx N_m$ is an extremely accurate approximation that we will use as needed. In this limit of small concentrations $c_S = N_S/N_m \ll 1$ we can also neglect the occurrence of a solute S having any other solutes as first and second neighbors; we thus only consider isolated solutes. Also in the limit of small concentrations $c_V = N_V/N_m \ll 1$, we can neglect the occurrence of vacancy-vacancy interactions in the host lattice. The binding of vacancies by the solutes creates vacancy-solute complexes of various types. Figure 2 shows the monovacancy/solute (VS) and divacancy/solute (VVS) complexes in an fcc lattice; we only consider mono- and di-vacancy/solute complexes in the present analysis. We label the various complexes by the index “i”, with each complex having n_i vacancies, an energy E_i , and g_i possible configurations of the vacancies. We then define the vacancy/solute complex binding energy as the energy relative to the formation energy E_V^f of the isolated vacancies in the host, $\Delta E_i = E_i - n_i E_V^f$. For example, in an fcc lattice, there are $g_i=12$ configurations having a single vacancy $n_i=1$ (Fig 2b), each configuration having energy $\Delta E_i = E_i - E_V^f$. For hcp lattices, there are two different solute/single-vacancy configurations corresponding to vacancies located in the basal plane of the solute and vacancies located in the basal planes above and below the basal plane of the solute, respectively.

A state of the system is then defined by the number N_V of vacancies in the host lattice away from the solutes and the numbers N_i of each type of vacancy/solute complex, with the total number of vacancies in the system given as $N_V^{tot} = N_V + \sum_i n_i N_i$. The energy of the state is then

$$E = N_V^{tot} E_V^f + \sum_{i=1} N_i \Delta E_i. \quad (1)$$

The number of distinct microstates associated with the given $\{N_V, N_i\}$ is found as follows. A single solute atom and its possible neighboring vacancy sites removes $\eta = 1 + \sum_{i \in VS} g_i$ atoms from the number of bulk lattice sites. The number of ways of distributing the N_V isolated vacancies among the remaining $N_{latt} - \eta N_S$ sites in the bulk lattice away from the solutes is

$$[\text{Number of states in host subsystem}] = \frac{(N_{latt} - \eta N_S)!}{N_V! (N_{latt} - \eta N_S - N_V)!}.$$

Each of the type i complexes is distributed among the N_S solutes, and the total number of ways to distribute them is

$$[\text{Number of states in solute subsystem}] = \frac{N_S!}{N_S - \sum_{i=1} N_i} \prod_{i=1} \frac{g_i^{N_i}}{N_i!}$$

where the $g_i^{N_i}$ term accounts for the number of ways to distribute the vacancies within each complex. The total number of microstates is then the product of the above two quantities, since the vacancies in the host and solute subsystems are independent. The partition function Z for the system is then $Z(N_V, \{N_i\}) = [\text{Number of microstates associated with } \{N_V, N_i\}] e^{-E/kT}$. Inserting Eq. 1, using the microstate counting above, and performing minor manipulations, gives the partition function as

$$Z = \frac{[N_{latt} (1 - \eta c_S)]!}{N_V! ([N_{latt} (1 - \eta c_S)] - N_V)!} e^{-N_V^{tot} E_V^f / k_B T} \frac{N_S!}{N_S - \sum_{i=1} N_i} \prod_{i=1} \frac{(g_i e^{-\Delta E_i / k_B T})^{N_i}}{N_i!}. \quad (2)$$

where $c_S = N_S / N_{latt}$ is the solute concentration in the lattice. The Helmholtz Free Energy A then follows as $A = -k_B T \ln(Z)$. Using Stirling's formula $\ln(N!) \approx N \ln(N) - N$ and defining the concentration of each complex as $c_i = N_i / N_{latt}$ yields

$$A = k_B T \left\{ \begin{aligned} & N_V^{tot} E_V^f / k_B T + ([N_{latt} (1 - \eta c_S)]) \ln([N_{latt} (1 - \eta c_S)]) - N_V \ln(N_V) + \\ & \left(N_S - \sum_{i=1} N_i \right) \ln \left(N_S - \sum_{i=1} N_i \right) + \sum_{i=1} [N_i \Delta E_i / k_B T + N_i \ln(N_i / g_i)] \end{aligned} \right\}. \quad (3)$$

The chemical potential μ_i of complex i is obtained as $\mu_i = dA/dN_i$, leading to

$$\mu_V = k_B T \left[\frac{E_V^f}{k_B T} + \ln \left(\frac{c_V}{1 - \eta c_S} \right) \right], \quad (4a)$$

$$\mu_i = k_B T \left[\frac{\Delta E_i + n_i E_V^f}{k_B T} + \ln \left(\frac{1}{g_i} \frac{c_i}{c_S - \sum_{i=1} c_i} \right) \right]. \quad (4b)$$

The above results are general; we have not yet specified any conditions on the system that will quantify the individual concentrations of the various complexes. We next apply this general thermodynamic model to the situation of interest - the partitioning of vacancies between the bulk and solute systems during aging.

At the effective solutionizing temperature T_S^{eff} , the system is considered to be in thermal equilibrium with the external environment. Vacancies can be annihilated and created at surfaces or other sources/sinks, which is equivalent to vacancies being in equilibrium with an external “gas” of vacancies, so that the chemical potential of a vacancy in the bulk lattice is $\mu_V = 0$. In equilibrium, the chemical potential of an individual vacancy in any complex is equal to the chemical potential of a vacancy in any other complex or the bulk lattice, $\mu_V = \mu_i = 0$. So, in thermal equilibrium, the solution of Eqs. 4 for the concentration of each complex at the effective solutionizing temperature is thus

$$c_V(T_S^{eff}) = (1 - \eta c_S) \exp[-E_V^f / k_B T_S^{eff}], \quad (5a)$$

$$c_i(T_S^{eff}) = c_S \frac{g_i \exp[-E_i / k_B T_S^{eff}]}{1 + \sum_{k=1} g_k \exp[-E_k / k_B T_S^{eff}]}. \quad (5b)$$

The total vacancy concentration, i.e. total number of vacancies divided by the number of lattice sites, inside the system at T_S^{eff} is then

$$c_V^{tot} = c_V(T_S^{eff}) + \sum_{i=1} n_i c_i(T_S^{eff}). \quad (6)$$

These results emerge from standard equilibrium thermodynamics and are not new.

Upon quenching below T_S^{eff} to some lower temperature, we now assume that (i) all the vacancies remain within the material, i.e. there is no further annihilation, and (ii) the vacancies repartition to remain in internal equilibrium among the bulk lattice and the various complexes. As noted earlier, annihilation involves comparatively long-range transport to traps and sinks, which is strongly inhibited below T_S^{eff} ⁴⁻⁷. Since the purpose of quenching is often to achieve a vacancy supersaturation, assumption (i) is thus valid. Redistribution of vacancies among the bulk lattice and complexes is achievable because this requires only vacancy transport over distances comparable to the average distance between solutes³. In fact, the existence of natural aging demonstrates that local transport of solutes, not just vacancies, is possible at low temperatures³. Thus, assumption (ii) is also valid.

With no further vacancy annihilation, the total vacancy concentration must equal the value at equilibrium (Eq. 6) at all times. With internal equilibrium, the chemical potentials of

vacancies in all complexes and bulk must be equal, so that the chemical potentials for the complexes satisfy $\mu_V = \frac{1}{n_i}\mu_i$. Along with Equations 4a,b and the overall constraint of Eq. 6, this relationship yields a closed set of equations for the individual concentrations c_V and c_i at all temperatures $T < T_S^{eff}$. Solving Eqs. 4a,b using $\mu_V = \frac{1}{n_i}\mu_i$ leads to the implicit relationship

$$c_i(T) = g_i \left(\frac{c_V}{1 - \eta c_S} \right)^{n_i} \left(c_S - \sum_{k=1} c_k \right) \exp \left[-\frac{\Delta E_i}{k_B T} \right]. \quad (7a)$$

Summing Eq. 7a over the complexes i , solving for the sum, and reinserting the result into Eq. 7a then yields

$$c_i(T) = c_S \frac{g_i \left[c_V / (1 - \eta c_S) \right]^{n_i} \exp[-\Delta E_i / k_B T]}{1 + \sum_{k=1} g_k \left[c_V / (1 - \eta c_S) \right]^{n_k} \exp[-\Delta E_k / k_B T]}. \quad (7b)$$

where only the unknown c_V remains on the right-hand side of Eq. 7b. The total number of vacancies remains as

$$c_V^{tot} = c_V(T) + \sum_{i=1} n_i c_i(T), \quad (8)$$

and is equal to Eq. 6. Substituting Eqs. 7b into Eq. 8 then yields

$$c_V^{tot} = c_V + c_S \frac{\left(\frac{c_V}{1 - \eta c_S} \right) \sum_{i \in VS} g_i \exp \left[-\frac{\Delta E_i}{k_B T} \right] + 2 \left(\frac{c_V}{1 - \eta c_S} \right)^2 \sum_{i \in VVS} g_i \exp \left[-\frac{\Delta E_i}{k_B T} \right]}{1 + \sum_{i=1} g_i \left(\frac{c_V}{1 - \eta c_S} \right)^{n_i} \exp[-\Delta E_i / k_B T]} \quad (9)$$

Eq. 9 is an implicit cubic polynomial with one real root for the unknown $c_V(T)$, which is the primary quantity of interest.

The binding of vacancies by the solutes reduces $c_V(T)$ as compared to $c_V(T_S^{eff})$, and this slows down vacancy-mediated diffusion processes. Precipitation processes limited by diffusion are thus retarded by the factor $R = c_V(T_S^{eff}) / c_V(T)$, computed directly from Eqs. 5, 6, and 9 as a function of the key parameters associated with vacancy/solute binding and solute concentration. A simplified form for R may be obtained by assuming the solute/divacancy population to be small,

$$\left(\frac{c_V}{1 - \eta c_S} \right) \sum_{i \in VS} g_i \exp \left[-\frac{\Delta E_i}{k_B T} \right] \gg 2 \left(\frac{c_V}{1 - \eta c_S} \right)^2 \sum_{i \in VVS} g_i \exp \left[-\frac{\Delta E_i}{k_B T} \right], \quad (10)$$

leading to

$$R = \frac{c_V(T_S^{eff})}{c_V(T)} \approx \frac{1 + c_S \left[\sum_{i \in VS} g_i \left(\exp[-\Delta E_i / k_B T] - 1 \right) - 1 \right]}{1 + c_S \left[\sum_{i \in VS} g_i \left(\exp[-\Delta E_i / k_B T_S^{eff}] - 1 \right) - 1 \right]}. \quad (11)$$

If the VS binding is moderately strong and the temperature T is much lower than T_S^{eff} , then an even simpler result emerges,

$$R = 1 + c_S \sum_{i \in VS} g_i \exp[-\Delta E_i / k_B T]. \quad (12)$$

The simplified expressions of Eqs. 11 and 12 for the retarding factor R provided a very easy first assessment of solute type (ΔE_i) and solute concentration (c_S) to achieve substantial delay of natural aging $R(T) \gg 1$ at the quench temperature but limited delay $R(T) \sim 1$ at the artificial aging temperature.

III. Mobility of solute/vacancy complexes

If binding of vacancies to solutes is to be effective in inhibiting diffusive processes, it is required that the diffusion of the complexes themselves be sufficiently slow, much slower than vacancy diffusion, and preferably comparable to or slower than the diffusion of the precipitation-forming solutes in the system.

We first assess the diffusion of the monovacancy/solute complex. The solute moves through a correlated motion involving not only solute-vacancy exchanges, but vacancy hops about the solute wherein the solute-vacancy diffusion rate is given as

$$D_{VS} = (a^2/6) [Probability\ of\ VS\ complex] [correlation\ factor] [V-S\ exchange\ rate].$$

a is the lattice parameter of the host material and the factor of $1/6$ is pertinent for fcc lattices. The probability of finding a VS cluster is given by its concentration, c_{VS} . The correlation factor accounts for motions that return to the original state without any net motion.

The diffusion of dilute solutes in a host metal is a classical problem within materials science which has been treated by the well-known 5-frequency model and gives the correlation factor¹⁰⁻¹³. The 5-frequency model considers five distinct jump frequencies W_i , $i=1, \dots, 5$, associated with vacancy hops relevant to solute motion as indicated in Figure 3. The five hops consist of the bulk vacancy migration (W_0), the “orbiting” of the vacancy around the solute (W_1), the vacancy/solute exchange (W_2), the hop of a vacancy away from the solute (W_3), and the hop of the vacancy toward the solute (W_4). Each vacancy “hop” has a migration path with migration enthalpy barrier H_i^m and associated transition frequency $W_i = \nu_i \exp[-H_i^m / k_B T]$ where ν_i is an attempt frequency. In accordance with the generic expression above, the diffusion coefficient of the solute-vacancy cluster in an fcc lattice is then written as

$$D_{VS} = a^2 c_{VS} f W_2 \quad , \quad f = \frac{2W_1 + 7W_3 F}{2W_1 + 2W_2 + 7W_3 F} \quad (13a)$$

where $(2/7) < F < 1$ is ^{14,15}

$$F = 1 - \left(\frac{1}{7} \right) \frac{10(W_4/W_0)^4 + 180.3122(W_4/W_0)^3 + 924.3303(W_4/W_0)^2 + 1338.0577(W_4/W_0)}{2(W_4/W_0)^4 + 40.1478(W_4/W_0)^3 + 253.3(W_4/W_0)^2 + 435.2839(W_4/W_0)} \quad (13b)$$

More generally, the form of f depends on the host crystal structure ^{10,13,16,17}.

It is useful to identify two limiting cases for D_{VS} . If vacancy/solute exchange is very fast ($W_2 \gg W_1$ and/or $\gg W_3$) then $D \sim 2W_1 + 7FW_3$. If vacancy/solute exchange is very slow ($W_2 \ll W_1$ and/or $\ll W_3$) then $D \sim W_2$ and diffusion is controlled by the exchange process. When precise results are not needed, it is then sufficient to capture these limiting cases with the approximation

$$D_{VS} = v a^2 c_{VS} f^{5\omega} e^{-H_{VS}^m / k_B T} \quad (14a)$$

where $1 < f^{5\omega} < 3.5^{10}$ and

$$H_{VS}^m = \begin{cases} H_2^m & \text{for } W_2 \ll W_1, W_3 \\ \min(H_1^m, H_3^m) & \text{for } W_2 \gg W_1, W_3 \end{cases} \quad (14b)$$

In cases where there is strong binding by the solute of multiple vacancies (limited here to the divacancy/solute complexes), the diffusion of such complexes must also be considered. It is well-known that divacancy diffusion itself is extremely fast, and there are several paths for divacancy/solute complex diffusion in which the complex remains un-dissociated. To our knowledge, there is no widely-held theory for divacancy/solute diffusion comparable to the 5-frequency model. However, the generic form of Eq. 13a, and hence Eq. 14a, provides guidance to write

$$D_{VVS} = v a^2 c_{VVS} e^{-H_{VVS}^m / k_B T} \quad (15)$$

where correlations are neglected but could be added if calculable. We then consider a mechanism for the complex in which the two vacancies are near-neighbors (Fig 3b), which tends to have the strongest divacancy/solute binding energy as shown later in Sec. IV. The migration process is envisioned to proceed in two steps. The first step is the migration of one vacancy to an adjacent site that remains a neighbor of both the solute and the other vacancy. We denote the rate for this step as W_1^{VVS} with migration enthalpy $H_{VVS(1)}^m$. The second migration step is the exchange of the solute with the vacancy. We denote the rate for the second step by W_2^{VVS} and the migration enthalpy by $H_{VVS(2)}^m$. Diffusion of the complex is controlled by the slower of the two processes, so that the relevant migration barrier is

$$H_{VVS}^m = \max \left[H_{VVS(1)}^m, H_{VVS(2)}^m \right]. \quad (16)$$

Within the above analysis, the applicability of the “diffusion-on-demand” concept requires that

$$D_V > D_{VS}, D_{VVS}. \quad (17)$$

where the vacancy diffusion is given by the standard result

$$D_V = \nu a^2 c_V e^{-H_V^m/k_B T}. \quad (18)$$

If the denominator in Eq. 7b is approximated as unity, the diffusion coefficients simplify to

$$D_{VS} = \nu a^2 g_{VS} c_V c_S e^{-\Delta E_{VS}/k_B T} e^{-H_{VS}^m/k_B T} \quad (19a)$$

$$D_{VVS} = \nu a^2 g_{VVS} c_V^2 c_S e^{-\Delta E_{VVS}/k_B T} e^{-H_{VVS}^m/k_B T} \quad (19b)$$

The second expression contains c_V but the binding of vacancies by solutes implies that the equilibrium concentration at the effective solutionizing temperature is an upper bound to c_V , $c_V < \exp(-E_V^f/k_B T_S^{eff})$. Using this upper bound allows further simplification of Eqs. 19 to

$$H_V^m < H_{VS}^m + \Delta E_{VS} - k_B T \ln[g_{VS} c_S] \quad (20a)$$

$$H_V^m < H_{VVS}^m + \Delta E_{VVS} + E_V^f \left(T/T_S^{eff} \right) - k_B T \ln[g_{VVS} c_S]. \quad (20b)$$

Eqs. 20 provides a rapid approximation for assessing the applicability of “diffusion-on-demand”.

IV. First-Principles Computation of Controlling Material Parameters

IVa. Methods

Spin-polarized density functional theory (DFT) with the Perdew-Wang-91¹⁸ generalized gradient approximation (GGA)¹⁸ and pseudopotentials constructed in self-consistent projector augmented-wave (PAW) framework¹⁹ as implemented in VASP were used for all calculations. A fully automatic Monkhorst Pack k-mesh generation scheme was used in which the Brillouin zone had 40 subdivisions in each direction and was shifted from the gamma center by 0.5^{20,21}. A kinetic energy cut-off of 400 eV was used for all host-solute pairs^{18,22}. Energy barriers were calculated using the Nudged Elastic Band (NEB) method^{23,24}. **Calculations were performed using fixed volume, and energy contributions due to any induced pressures were verified to be negligible in all cases.** Relaxation calculations were converged to 10⁻⁴ eV and nudged elastic band to 0.1 eV/Å. All monovacancy binding energies were calculated using an fcc-Al (3x3x3) cubic cell, divacancy binding energies an fcc-Al (4x4x4) cubic cell, and NEB calculations in the same cells. Monovacancy binding energies were calculated as the energy difference between the

vacancy at a near-neighbor site of the solute and at a third neighbor site of the solute. Divacancy binding energies were calculated as the energy of moving two vacancies from the isolated vacancy state to a solute species. Solute-vacancy binding was investigated in Mg using an hcp 4a x 4a x 3c simulation cell.

IVb. Vacancy/Solute binding energies

The thermodynamic model developed here reveals the controlling material property for the “diffusion on demand” principle to be the solute-vacancy binding energy ΔE_{VS} (eqn 12). We have calculated the binding energy for a wide range of solutes at the nearest and next-nearest neighbor positions and show them as a function of Pauling electronegativity (pEN) in Figure 4. Nearest-neighbor binding energies correlate with pEN, showing it is mainly controlled by electronic factors. The next-nearest neighbor binding does not correlate with pEN while previous calculations have shown that it correlates with misfit volume indicating control by mechanical factors²⁵. The results in Figure 4 show that next-near-neighbor binding is much weaker than nearest-neighbor binding²⁵. The neglect of next-near-neighbor binding in our model is thus a good approximation.

We have also computed the solute/divacancy binding energies for a selection of solutes (Ti, Cr, Fe, Ga, Sn, and Pb) spanning the range from repulsive to attractive solute/vacancy binding. The divacancy binding energies as a function of pEN are shown in Figure 5. As with monovacancy binding, increasing solute electronegative correlates with stronger binding of multiple vacancies. However, the divacancy binding energies are strongly configuration-dependent. Those solutes with strong monovacancy binding also show stronger binding of near-neighbor divacancies. Conversely, solutes with strong monovacancy repulsion have lower energies for the separated divacancy configurations. Thus, solutes useful for “diffusion on demand” based on ΔE_{SV} tend to have a strong near-neighbor divacancy/solute complex binding. Such solutes could thus bind additional vacancies, enhancing the retardation effects. However, such divacancy/solute complexes may not release the vacancies at artificial aging temperatures or they may diffuse too rapidly. This highlights the need for the careful consideration of both monovacancy and divacancy binding energies, computed here, and migration energies, computed in the next subsection, of the various vacancy/solute complexes in each candidate system.

IVc. Vacancy/Solute complex migration barriers

We now examine the activation barriers to the motion of solute-vacancy complexes shown in Figure 3. The activation barriers for the elementary hops (W_1 , W_2 , W_3 , W_4) in the solute/vacancy complexes are shown in Figure 6, again versus pEN and for selected solutes. Stronger vacancy binding corresponds to lower barriers for solute-vacancy exchange (W_2) and vacancy capture (W_4), the latter fully expected; weaker vacancy binding corresponds to higher barriers for vacancy orbit (W_1) and vacancy escape (W_3). Based on these migration energies and the 5-frequency model, solutes having stronger binding to vacancies will migrate based on a concerted vacancy-orbit/solute-vacancy exchange, $D \sim a^2 c_{VS} (2W_1 + 7FW_3)$, while solutes having weaker binding will migrate based on a vacancy-orbit/vacancy-capture/release mechanism, $D \sim a^2 c_{VS} W_2$. In both cases, the migration barrier to solute-vacancy diffusion is always higher than the migration barrier for vacancy diffusion in the bulk.

Figure 7 shows the computed migration barriers for the elementary hops associated with the diffusion of the near-neighbor-divacancy/solute complexes, again versus pEN for consistency. For strong divacancy binding, the vacancy orbit migration energy becomes large and limits diffusion. For weak divacancy binding, the solute-vacancy exchange migration energy becomes large and limits diffusion. The migration barrier for solute-divacancy diffusion is therefore also always higher than the migration barrier to divacancy diffusion in the bulk.

Whether solute diffusion is slow enough such that precipitation kinetics are controlled by the factor R requires that $D_V \gg D_{VS}, D_{VVS}$. This requires knowledge of the migration barriers and the vacancy and solute/vacancy complex populations. In the following section we will assess a few representative solutes for their suitability for “diffusion on demand”.

V. Diffusion-on-Demand: application of the model

We now have calculated all the necessary materials parameters to determine the types and concentrations of solutes that could achieve the desired “diffusion on demand” (ΔE_{VS} , Fig. 4; ΔE_{VVS} , Fig. 5; various H^m , Figs. 6 and 7). The computed solute-vacancy binding energies ΔE_{VS} suggest Ga, Sn, and Pb as candidate solutes that span the range of potentially feasible binding to achieve “diffusion-on-demand”. In practice, neither Ga nor Pb would likely be used in Al - Ga is a known embrittler of Al^{26,27} and Pb has very low solubility^{28,29}. In spite of practical considerations, these three elements provide realistic materials parameters for exercising the model. We test our model using Ga, Sn, and Pb around/below expected solubility limits and under realistic processing conditions of natural aging at $T=293\text{K}$ and artificial aging at $T=443\text{K}$. The effective solutionizing temperature is not well-established, and depends on microstructure and quenching rates since vacancies are annihilated at sinks such as grain boundaries and surfaces during the early stages of quenching⁸. The effective solutionizing temperature is meant to capture the quenched-in vacancy population and will therefore always be lower than experimental solutionizing temperatures, which are typically 800K or larger. We thus investigate a range of values $T_s^{eff} = 500, 600, 700, 800\text{K}$ to assess the sensitivity of the predictions to this quantity.

We first verify that vacancy transport is controlled by the residual bulk vacancies, for the Ga, Sn, and Pb solutes, i.e. Eqs. 17 are satisfied. Figure 8 shows the ratio $D_V/(D_{VS}+D_{VVS})$ for Ga, Sn, and Pb with the above representative processing parameters. Even with the reduced vacancy concentration in the lattice as a result of vacancy binding at the solutes, the vacancy diffusion is many orders of magnitude faster than the diffusion of all solute complexes. $D_V/(D_{VS}+D_{VVS}) \gg 1$ means that bulk vacancies control vacancy mediated diffusion and that “diffusion on demand” is possible.

Having established the possibility of “diffusion on demand” for these solutes under realistic processing conditions, we now examine the retarding factor R achievable for these solutes. Using the thermodynamic model of Eqs. 5, 6, and 7, we compute the retarding factor R versus solute concentration for the representative conditions. For Ga (Figure 9), the solute-vacancy binding is so weak such that $R \sim 1$ under all conditions; Ga is thus ineffective for “diffusion-on-demand”. For Sn (Figure 10), the solute-vacancy and solute-divacancy binding energies are higher and so, for Sn concentrations around the solubility limit of $\sim 100\text{ ppm}$, we predict $R \sim 10\text{-}20$ under natural aging and $R < 1.5$ at artificial aging. Thus, at sufficiently high concentrations (e.g. $\geq 40\text{ ppm}$), Sn is a viable solute for achieving valuable diffusion-on-demand

at sufficient concentrations. For Pb (Figure 11), the very strong binding of vacancies and divacancies leads to $R \sim 10^3 - 10^4$ for natural aging and $R \sim 10$ under artificial aging at concentrations of 10-20 ppm. Thus, for Pb, there can be a substantial delay of natural aging but only at the cost of a substantial delay under artificial aging. For lower Pb concentrations more likely in the range of Pb solubility (< 5 ppm), the predictions for R at the natural aging temperature drop precipitously and depend strongly on the effective solutionizing temperature. Thus, while Pb has the possibility of “diffusion-on-demand”, the model predicts that R is very sensitive to the precise conditions (concentration and effective solutionizing temperature) that are unlikely to be controlled/known with high accuracy. Thus, while under some conditions Pb could achieve useful “diffusion-on-demand”, practical issues suggest that achieving well-defined delay of precipitation kinetics would be difficult. Overall, for natural aging temperatures around 293 K and artificial aging temperatures of 443 K, we conclude that a vacancy binding energy in the range of 0.2 to 0.3 eV and with moderate solubility (100 ppm) provides conditions for viable “diffusion-on-demand” in Aluminum.

Pb solutes strongly bind divacancies and also have low solubility. These two features are presumably related and thus probably arise in many different systems. The predicted behavior of Pb thus merits further analysis since other strong-binding solutes (e.g. Bi in Al) could show similar response. At the effective solutionizing temperature, a significant number of Pb solutes may already bind a number of divacancies, thus making those Pb solutes unable to absorb more vacancies upon quenching. Furthermore, if the concentration of quenched-in vacancies exceeds twice the concentration of dissolved solutes, i.e. if $c_V(T_S^{eff}) > 2c_S$, then the Pb solutes are unable to absorb all of the vacancies and the residual vacancy concentration remains comparable to the original quenched value. These qualitative expectations are revealed more clearly by examining the predictions for Pb carefully over solutionizing temperatures between 600K and 800K, at natural aging ($T=293K$). Figure 12 shows the fraction of Pb solutes occupied by two vacancies, c_{VVS}/c_S , and the retarding factor R versus Pb solute concentration c_S at various effective solutionizing temperatures. For higher values of effective solutionizing temperatures (more initial vacancies) and/or lower solute concentrations c_S , the ratio c_{VVS}/c_S approaches unity, and the values of R decrease rapidly toward $R \sim 1$. The steep drop in R occurs precisely where the number of solutes is insufficient to absorb (nearly) all of the vacancies. Thus, strong solute/vacancy and/or solute/divacancy binding, which is likely associated with low solute solubility, leads to results for R that can change dramatically over a narrow range of concentration and effective solutionizing temperature. This regime is undesirable for reliable material processing and uncertain achievement of controlled “diffusion-on-demand”.

The predictions of the full model as shown in Figures 9-11 are not too difficult to compute, but a simplified model provides a means for rapid assessment with limited inputs. Figures 9-11 thus show the predictions of simple model $R = 1 + c_S \sum_{i \in VS} g_i e^{-\Delta E_i/k_B T}$ (Eq. 12), which is independent of effective solutionizing temperature and neglects solute-divacancy binding. The simple model correctly predicts that Ga is not useful for “diffusion-on-demand”, with $R \sim 1$ (Figure 9), with differences with the full predictions being quantitatively negligible. More importantly, the simple model proves to be quite accurate – within a factor of 2 – for Sn over a wide range of solute concentrations (Figure 10) and for effective solutionizing temperatures. For Pb, the simple model generally underestimates R by an order of magnitude or more, since strong solute-divacancy binding controls the behavior in Pb. We conclude that the simplified model for R is of good practical utility for assessing the prospects for “diffusion-on-

demand” for a given solute in a given matrix, making it useful as a predictive materials design tool to identify candidate solutes for controlling precipitation kinetics.

In a recent publication, it has been demonstrated experimentally that Sn indeed delays natural aging in Al-Mg-Si without significantly affecting artificial aging³⁰. Here, we revisit the comparison of the simplified model with experimental data. Figure 13 shows the predictions of the simple model for R for Sn solutes at concentrations in the range 40-100 ppm and at both natural and artificial aging temperatures. At the natural aging temperature, the model underpredicts the measured R values by a factor of ~ 10 . This difference is of practical significance, but the model uses only computed results with no fitting parameters and captures the general trend. There is also some scatter in the experimental results, reflecting the difficulty in measuring R precisely from evolution of the hardness versus time, although this does not account for the factor of ~ 10 deviation between theory and experiment. In light of this difference, we consider whether the experimental results can be predicted using a modified value of the vacancy/solute binding energy, ΔE_{VS}^{exp} . Figure 13 shows the predictions for R corresponding to $\Delta E_{VS}^{exp} = -0.30$ eV, which is 0.06 eV larger (more negative) than the DFT-computed value; the agreement is very good over the entire range of values. The 0.06 eV difference between computed and fitted binding energies is outside the accuracy of DFT. However, the DFT results are computed at $T=0$ K and it remains possible that thermal effects may play some role. Also, the DFT is performed in pure Al, without the additional alloying components of the real materials, which may shift chemical potentials for defect energies by small amounts. For the purposes of design and solute selection to achieve “diffusion-on-demand”, we would recommend use of the standard DFT at $T=0$ K with attention to more subtle details for prediction refinement implemented on an as needed basis.

VI. Discussion & Conclusions

The present work establishes a procedure for the selection of solutes for “diffusion on demand”:

- (i) Calculate candidate solute-vacancy binding energies (ΔE_{SV} , Fig 4) to determine if candidates demonstrate merit according to $R = 1 + c_S \sum_{i \in VS} g_i e^{-\Delta E_i/k_B T}$;
- (ii) For promising candidates, calculate the divacancy binding energies and migration barriers of vacancies and solute-vacancy complexes (Fig 5, 6, 7) to determine the applicability according to $D_V/(D_{VS}+D_{VVS}) \gg 1$ (Fig 8);
- (iii) Determine the solubility of promising candidate solutes at the solute levels required to achieve useful R values;
- (iv) Refine the model inputs and examine sensitivity of the computed R values to the computed material properties as needed.

Computed solute-vacancy binding energies here (Table 1) and elsewhere^{9,11,25} reveal Sn to be useful for “diffusion on demand” in Al, with possible applicability of Y (Table 1). Literature computations for In suggest it as another attractive candidate for $(\Delta E_{VS} = -0.2$ eV)²⁵. Prospects for Al-6xxx are limited, but the few viable solutes provide the desired performance.

The “diffusion-on-demand” concept and formalism developed here is general and has applicability outside of Al-6xxx. In particular, Mg is another host metal for which precipitation hardening is widely utilized³¹ and for which the hardening begins in a matter of hours³². Magnesium alloys utilize precipitates of MgAl, rare earth compounds, MgYNd, MgTh, and

others. If suppression of natural aging is desirable in these systems “diffusion-on-demand” may be a useful strategy. Table 1 shows the computed values of ΔE_{VS} for a variety of solutes in Mg. Mn has extremely strong binding, and may therefore bind vacancies even under solutionizing conditions, prohibiting the vacancy capture and release process at the heart of “diffusion on demand”. Several other solutes (Ni, Co, Rh) demonstrate binding that is lower than Sn in Al but sufficient to generate reasonable R at natural aging and $R \sim 1$ at artificial aging. These preliminary results suggest that “diffusion on demand” in Mg is achievable and that a search for optimal solutes based on the strategy described above could provide an improved set of candidates to implement the principle there.

In summary, we have presented a concept and model for the controllable delay of natural aging without affecting artificial aging. Predictions and trends of the model have been demonstrated in application to Al, showing that 10-100 ppm of solutes with solute-vacancy binding energies of 0.2-0.3 eV achieve the desired goals. We have shown that a simplified model works well, allowing for fast assessment of various solutes. The model can be extended to multiple solutes acting simultaneously, and applies to any system where quenched vacancies facilitate precipitate nucleation and growth.

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Figures

Figure 1. Schematic of solute-vacancy binding vacancies at various temperatures: (a) At the effective solutionizing temperature, the system is in thermal equilibrium which determines the total number of vacancies in the system; (b) after quenching to the natural aging temperature, many vacancies become bound to nearby solutes, reducing the number of vacancies in the bulk lattice available to drive kinetic aging processes under natural aging; (c) upon heating to artificial aging temperature, many vacancies are released back into the bulk lattice, becoming available for driving of kinetic aging processes. Green: host metal atoms; grey: solute atoms; Dashed empty circles: vacancies; dashed hexagons identify near-neighbor metal sites of the solute atoms.

Figure 2. Schematic showing possible solute-vacancy complexes in an fcc lattice: solute atom with (a) no vacancy; (b) a single vacancy; (c) two vacancies adjacent to one another; (d) two vacancies separated by $a/2[2,1,1]$; (e) two vacancies separated by $a[1,1,0]$; and (f) two vacancies separated by $a[1,0,0]$. g_i values indicate the number of identical configurations of each type; n_i values indicate the number of vacancies in each configuration.

Figure 3. Vacancy motions resulting in diffusion of solute-vacancy complexes in an fcc lattice: (a) diffusion paths in the "five frequency model" for solute-vacancy pairs are W_0 (bulk vacancy motion), W_1 (vacancy-solute orbit), W_2 (solute-vacancy exchange), and W_3 / W_4 vacancy escape / capture; (b) diffusion paths for solute-divacancy motion are W_1^{vv} (divacancy orbit) and W_2^{vv} (solute-vacancy exchange).

Figure 4. Solute-vacancy binding energy (ΔE_{vs}) in Al versus Pauling electronegativity (pEN). The solute-vacancy configurations are shown (colors matched with binding energies). Black dashed line: $\Delta E_{vs}=1.370-0.786 \times pEN$ least-squares fit to the nearest neighbor data. Dashed blue line: $\Delta E_{vs}=0$.

Figure 5. Solute-divacancy binding energy (ΔE_{vvs}) versus Pauling electronegativity (pEN), for selected solutes in Al. The various distinct solute/divacancy configurations are shown with colors matching with symbols for corresponding binding energies.

Figure 6. DFT-computed migration barriers H_i^m for solute-vacancy motions versus Pauling electronegativity (pEN). Horizontal dashed line: migration barrier for bulk vacancy diffusion¹¹. Motions are shown in Fig 3a, colors mapped with migration barriers.

Figure 7. DFT-computed migration barriers $H_{VVS}^m(i)$ for solute-divacancy motions versus Pauling electronegativity (pEN). Horizontal dashed line: activation barrier for diffusion of a divacancy in the bulk^{33,34}. Motions are shown in Fig 3b, colors mapped with migration barriers.

Figure 8. Ratio of bulk vacancy diffusion to solute-vacancy complex diffusion, $D_V/(D_{VS}+D_{VVS})$, versus solute concentration c_s , for solutes Ga, Sn, and Pb. Green, $T=293$ K (natural aging); Blue, $T=443$ K (artificial aging). Symbols indicate effective solutionizing temperatures (diamonds, $T_s^{\text{eff}}=600$ K; triangles, $T_s^{\text{eff}}=600$ K; circles, $T_s^{\text{eff}}=700$ K; squares, $T_s^{\text{eff}}=800$ K).

Figure 9. Predicted retarding factor R versus solute concentration c_s , for the solute Ga at natural aging (Green, $T=293$ K) and artificial aging (Blue, $T=443$ K), and for various effective solutionizing temperatures (diamonds, $T_s^{\text{eff}}=500$ K; triangles, $T_s^{\text{eff}}=600$ K; circles, $T_s^{\text{eff}}=700$ K; squares, $T_s^{\text{eff}}=800$ K).

Figure 10. Predicted retarding factor R versus solute concentration c_s , for the solute Sn at natural aging (Green, $T=293$ K) and artificial aging (Blue, $T=443$ K), and for various effective solutionizing temperatures (diamonds, $T_s^{\text{eff}}=500$ K; triangles, $T_s^{\text{eff}}=600$ K; circles, $T_s^{\text{eff}}=700$ K; squares, $T_s^{\text{eff}}=800$ K).

Figure 11. Predicted retarding factor R versus solute concentration c_s , for the solute Pb at natural aging (Green, $T=293$ K) and artificial aging (Blue, $T=443$ K), and for various effective solutionizing temperatures (diamonds, $T_s^{\text{eff}}=500$ K; triangles, $T_s^{\text{eff}}=600$ K; circles, $T_s^{\text{eff}}=700$ K; squares, $T_s^{\text{eff}}=800$ K).

Figure 12. Predicted R and predicted fractional occupancy of solute-divacancy complexes c_{vvs}/c_s versus solute concentration c_s for Pb solutes at $T=293 \text{ K}$ (natural aging) for various effective solutionizing temperatures between 600K and 800K as indicated. Note the steep decrease in R when the solute-divacancy complexes are saturated, $c_{vvs}/c_s=1$, which arises when the concentration of initial vacancies exceeds the capacity of the solutes to absorb the vacancies.

Figure 13. Measured versus predicted R for Sn in Al, using simplified model ($R = 1 + c_s \sum_{i \in \text{VS}} g_i e^{-\Delta E_i / k_B T}$). Blue symbols: results using DFT-computed solute-vacancy binding energy; Red symbols: results using a fitted value of the solute-vacancy binding energy. Solid symbols: artificial aging; Open symbols: natural aging.

Solute in Al	$\Delta E_{vs}(X)$ in	Solute in Mg	$\Delta E_{vs}(X)$ in-basal with Mg	$\Delta E_{vs}(X)$ out-of-basal with Mg
Bi	-0.42142	Mn	-0.91403	-0.91534
Pb	-0.41456	Ni	-0.17526	-0.06033
Sn	-0.25062	Co	-0.18638	-0.04071
Y	-0.13107	Rh	-0.15629	-0.04341
Ag	-0.12415	Bi	-0.09175	-0.10031
Ga	-0.08655	Pd	-0.11282	-0.05194
Pd	-0.07057	Pb	-0.06496	-0.07221
Zn	-0.06772	Cu	-0.07903	-0.04319
Ni	-0.04565	Ag	-0.04745	-0.03713
Cd	-0.02243	Cd	-0.04046	-0.04166
Cu	-0.01619	Sn	-0.03008	-0.03954
Rh	-0.01043	Zn	-0.03143	-0.02548
Co	-0.00275	Ru	-0.07666	0.02345
Ge	0.03469	Ge	-0.02446	-0.02259
Fe	0.09583	Ga	-0.00903	-0.00977
Ru	0.09989	Fe	0.01439	
Sc	0.11892	Y	0.08251	
Mn	0.18036	Tc	0.05417	
Tc	0.23273	V	0.1477	
Zr	0.25016	Sc	0.1722	
Cr	0.27242	Ti	0.22111	
Ti	0.33900	Mo	0.20964	
Mo	0.35790	Nb	0.31963	
V	0.37471	Cr	0.12741	
Nb	0.40910			

Table 1. Explicit listing of DFT calculated solute-vacancy binding energies (ΔE_{vs}) for various solutes in Al and Mg. Mg is hcp and has two possible vacancy binding sites, in the basal plane of the solute (first column, g=6) and out of the plane (second column, g=6).

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