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Chapter

Structural Disorder as Control of Transport Properties in Metallic Alloys

Eric R. Kaiser and Yong W. Kim

Abstract

Structural disorder is ubiquitous for a large class of metallic alloys. Such an alloy's transport properties are highly susceptible to change when the disorder is modified. A first-principle method has been developed for modeling of disorders in metallic alloys. In this approach, an alloy specimen is regarded as a randomly close-packed mixture of a population of nanocrystallites and constituent atoms in glassy state. The disorder is then represented by the size distribution function of the nanocrystallites. Under sustained exposure to thermal, stress, nuclear or chemical forcing at an elevated temperature, the distribution function becomes modified, and this process is predictable for a given forcing condition, and thus controllable. Transport of excitations is affected by the detail of the distribution function, making it possible to control transport properties, all at a fixed alloy composition. The modeling and experimental support will be presented.

Keywords: structural disorder, transport property, metallic alloys, thermal forcing

1. Modeling of structural disorder in alloys by nanocrystallites

Structural disorder is common in solid materials of daily use in general. The situation is particularly true of metallic alloys that define the scope and functionality of the myriad objects and structures that are devised of such alloys. The appropriate properties of metallic materials range from their intrinsic strength, resistance against shape change, the wide span of dimensions a metal may be worked into, myriad ways metallic objects may be assembled into different structures, wide temperature spans a metallic object may stably exist for a long period of time to the wide range of heat transport such metallic media can sustain. The listing of different thermophysical properties of metallic alloys appropriate for these applications can be rather extensive. In the great majority of cases, the regularity in the assembly of constituent atoms into a solid specimen plays a critical role. The degree of such regularity determines the material's ability to define its thermophysical properties. All of these properties are subject to structural disorder in the given metallic alloy medium.

Our group has formulated the world's first modeling approach to disordered metallic alloys in the past few years [1]. Each material specimen is modeled as a randomly-close packed assembly of constituent atoms in glassy state and an ensemble of nanocrystallites varying in size as large molecules. There is, however,

no single canonical view of the state of random close packing for a given material specimen but only a statistical view [2]. In order to help sharpen the scope of the disorder in alloys we have utilized a surrogate macroscopic material specimen in a two-dimensional assembly of steel spheres. The simulated material specimen is thermalized by driving the assembly in two mutually orthogonal directions by two independent stepping motors under digital control. The motors are driven by using a sequence of instructions derived from a chaotic algorithm. The simulated material specimen is continuously video imaged as a function of time, which is then analyzed for particle positions; the entire field of view is analyzed and reconstituted into a movie as a function of time. Analysis of the resulting sequence of particle positions shows that some of the single particles cluster into, and break out of, nanocrystallites in time. We thus obtain as a function of time the size-resolved distribution of nanocrystallites that are randomly close packed with single glassy particles in the simulated alloy medium. The size distribution is found to be stationary at each given intensity setting of the drive.

Operation of the digitally controlled drive of the simulated alloy specimen is fine tuned in such a way that the distribution of single particle velocities becomes Maxwellian to a high degree. When the digital drive intensity is changed, the single particle velocity distribution broadens or narrows linearly with the drive intensity to a good approximation. This feature provides the means to vary "the temperature" of the simulated specimen. The significant and interesting find is that the nanocrystallite size distribution function shows significant changes as the effective temperature of the simulated specimen increases. Here we find a nanocrystallite when it is composed of three or more particles where each constituent particle is in contact with two or more other particles within the nanocrystallite. The shape and size of nanocrystallites within the simulated alloy specimen change as a function of time but the average population of nanocrystallites maintains a stable functional form as a function of nanocrystallite size as defined by the number of constituent single particles.

2. Equilibrium nanocrystallite size distribution

The theoretical modeling formalism is thus constructed by means of the law of mass action. Nanocrystallites are regarded as large molecules that are mixed in the sea of single glassy particles. In the course of local fluctuations, nanocrystallites grow larger by merging or attachment, or become smaller by losing peripheral particles or breaking up into smaller nanocrystallites. This process maintains a detailed balance throughout over long time, much like the dissociation equilibrium in a gas medium consisting of large molecules mixed in a gas of monatomic particles.

As the medium temperature is increased toward the melting point of the given alloy, the population of nanocrystallites undergoes rapid large changes per unit change in temperature. Overall, nanocrystallites decrease in number density, and the medium becomes more populated by single atoms in glassy state. This pattern of temperature dependence is universal throughout metallic alloys. We model this phenomenon as equilibrium dissociation of nanocrystallites in the randomly close packed medium of glassy atoms and nanocrystallites in equilibrium.

By means of this theoretical framework, the temperature dependence of nanocrystallite populations has been computed for 44 different metals. They all follow the pattern of temperature dependence as outlined above. There are, however, small but distinct differences in these patterns of temperature dependence that are particular to the atomic properties of given metals. In order to formulate a realistic first order theory of alloys, we proceed to quantify the differences by grouping different alloys, according to their crystalline symmetry properties.

In this modeling we aim to model the nanocrystallites of different metals as realistically as known in solid state alloy literature. We first assert that all nanocrystallites are spherical in shape. Each nanocrystallite is cookie-cut out of the large lattice of the given alloy in such a way that the sphere of given radius contains the number of atoms in each given nanocrystallite. Since there are one or more ways this operation may be carried out depending on the crystalline symmetry property of the given alloy, all different versions of the sphere are considered in the subsequent dissociation potential calculations, and their average is taken in the final lookup table of dissociation potentials of atoms on the surface of each nanocrystallite. The interaction potentials between all possible pairs of atoms found in the nanocrystallite are calculated according to the interaction potentials of Lennard-Jones (L-J) type that have been obtained from quantum chemistry computation [3]. The L-J potentials are applied to find the dissociation potential for each of the atoms on the periphery of each given nanocrystallite in question. The dissociation potential computed in this manner grows larger asymptotically with increasing size of the nanocrystallite; the computed results are best fitted into a lookup table of dissociation potentials as a function of nanocrystallite size [1]. Individual values of the dissociation potential are obtained from the look-up table for the law of mass action calculation for the alloy in equilibrium.
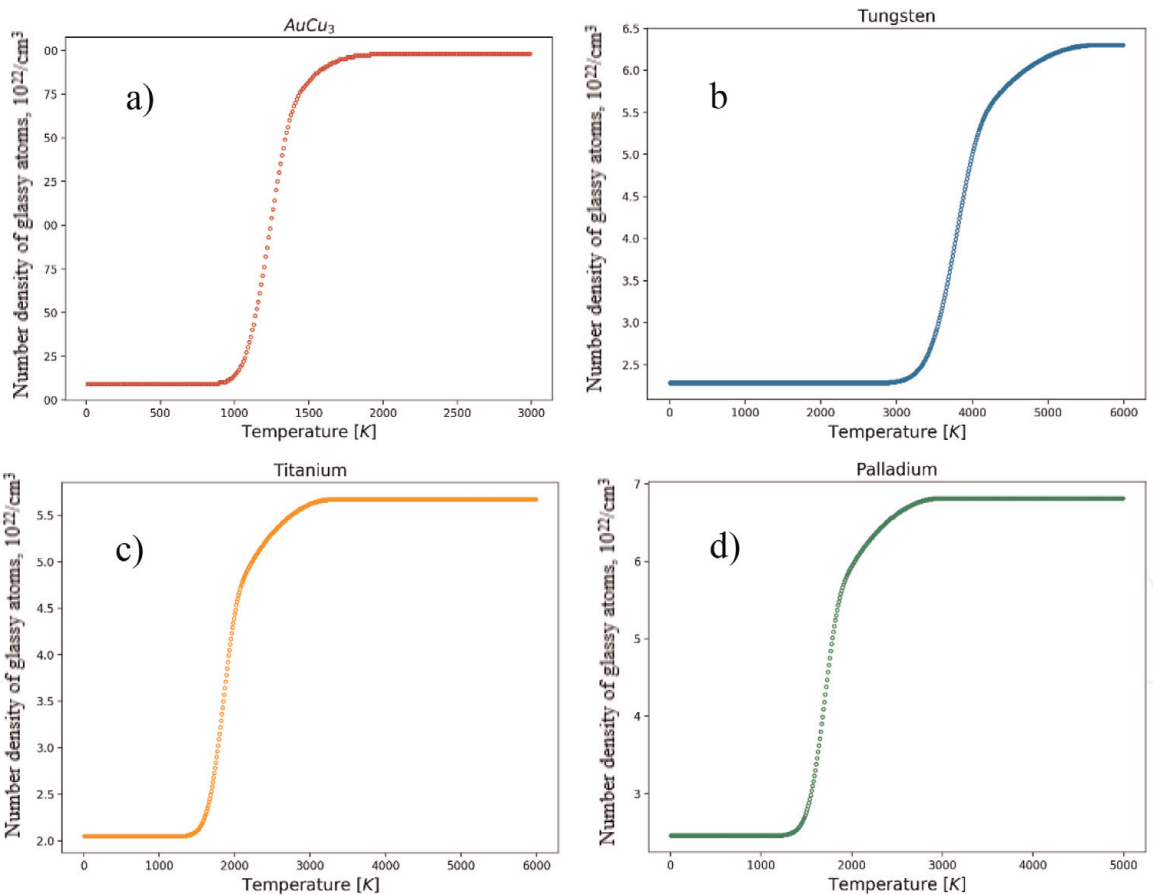

Figure 1.
Calculated number of glassy state atoms per cc as a function of temperature for: (a) binary alloy—$AuCu_3$ (1240.5 K); (b) BCC—tungsten (3695 K); (c) HCP—titanium (1948 K); and (d) FCC—palladium (1828 K). The melting points of the metals are listed in the parentheses. Operationally, we take the melting point to be at midpoint between the minimum and the maximum of the number density of glassy atoms, and this is in good agreement with the known data. By taking the midpoint between the maximum and the minimum number density. At room temperature when the population of nanocrystallites is largest, in each plot the number density of glassy state atoms starts off at the particular value, corresponding to its own randomly close packed state. In the case of $AuCu_3$ the number density of glassy state atoms at room temperature is 4.1×10^{22} atoms per cm^3. The rest of the atoms are tied up in the form of nanocrystallites with the degree of crystallinity at 0.314; the number of glassy state atoms increases to 5.98×10^{22} atoms per cm^3 when the specimen is fully molten [4].
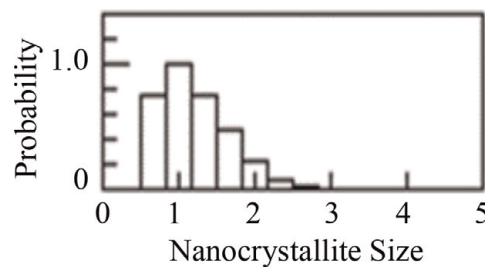
Figure 2.
Histogram by size of nanocrystallites of the single-element alloy at room temperature. Both the size axis (horizontal) and the probability axis (vertical) are shown in dimensionless form, the size as a fraction of the maximal size and the probability in fraction of the probability at the maximal size [1].

The result of such a calculation is shown in **Figure 1** for a gold-copper alloy. The calculation is carried out for the specimen of 1 cm^3 in volume. At room temperature, the degree of crystallinity is 0.314. The crystalline part of the specimen is in the form of nanocrystallites, whose size distribution function is shown in the histogram shown in **Figure 2**. The law of mass action is written out for each group of nanocrystallites of given size. Using the look-up table of dissociation potentials as a function of nanocrystallite size, the full complement of the coupled dissociation equations are solved numerically to find the number of atoms in glassy state as a function of temperature. The detailed procedure of iterative computation is described in detail elsewhere [1].

A perusal of **Figure 1** shows that the equilibrium population of glassy state atoms grows larger with increasing temperature for all different forms of metallic materials. The range of active temperature dependence is centered about the respective melting point in the form of a hyperbolic tangent function when the zero-crossing point of the function is aligned with the point of maximal slope. In fact, the temperature at which the slope of the function maximizes has a close match with the known melting point of the alloy [1]. On the other hand, there are a couple of small but definite differences among the four groups of alloys represented in **Figure 1**: one, the computed population of glassy atoms versus temperature is not symmetric about the maximal slope point; and two, the asymmetry varies on average according the crystalline lattice symmetry property of each given group of metals. We recognize that the asymmetry is reminiscent of the manner in which dissociation of molecules undergo in molecular gases or in plasma of gas mixtures of molecules and atomic gases as a function of temperature [1].

We have thus explored ways in which all groups of alloys of interest may be represented by a single function for the manner in which these alloys undergo structural transformation under thermal forcing. The hyperbolic tangent function is rewritten in such a way that the argument switches from one scaling with temperature below the melting point to another above it, and it is shifted upward so that its value remains bounded between zero and a positive constant.

3. Response of nanocrystallites to heating: a first order representation

The law of mass action calculation shows that when the temperature is increased through the melting point, the number of glassy atoms in the alloy specimen increases in the form of hyperbolic tangent (see **Figure 1**) to reach an asymptotic value in the limit of full melting. This pattern holds for all 44 metals for which the computation has been carried out (38 pure metals and six alloys) [5]. There are small but noticeable deviations from the ideal hyperbolic tangent profile: one, the functional form of the changing glassy atom population as a function of temperature is not exactly symmetric about the melting point; and two, the asymmetry is

dependent on the symmetry group of the metals. The width to melting temperature ratio is 0.139 ± 0.012 for BCC metals, 0.160 ± 0.010 for FCC, 0.177 ± 0.008 for HCP and 0.161 ± 0.016 for binary alloys. The two deviations mentioned above appear to reflect the groupings of the asymmetry.

The general shape of the number density of glassy atoms as a function of temperature rises from the glassy atom density at room temperature (n_0) to the maximum value (n_{max}) past the melting point. The results shown in **Figure 1** are found from the system of the law of mass action equations; the number density of glassy atoms is always positive. The functional relationship may be well represented by the hyperbolic tangent function with the following modification:

$$n_g(T) = \frac{n_{max} + n_0}{2} + \frac{n_{max} - n_0}{2} tanh\left[s(T)(T - T_{mp})\right] \quad (1)$$

Note that $n_{max} = n_0 + \sum_{j=3}^{j_{max}} j n_{nanocrystallite}(j)$, where $n_{nanocrystallite}(j)$ denotes the number density of j-atom nanocrystallites at room temperature. $s(T)$ is a switching function introduced in order to model the asymmetry in the glassy atom density about the melting point:

$$s(T) = \begin{cases} \eta, & T < T_{mp} \\ \lambda T_{mp}/T, & T \geq T_{mp} \end{cases} \quad (2)$$

Here η and λ are fitting constants for the computed glassy atom density versus temperature plot; they vary from one metallic specimen to another. T_{mp} denotes the melting point.

The goal here is to find a set of fitting parameters that will accurately capture the shape of all nanocrystallite species within each crystalline symmetry group (i.e., FCC, BCC, HCP and binary). We first normalize the fit with the following by introducing $T^* = T/T_{mp}$, $n^* = [n_g(T) - n_0]/(n_{max} - n_0)$ and $s^* = s(T) T_{mp}$. The fit to the computed glassy atom density becomes

Crystalline Symmetry	η^*	λ^*	Metals
FCC	8.84 ± 0.48	5.37 ± 0.32	Ag, Al, Au, Ca, Ce, Cu, Ir, Ni, Pb, Pd, Pt, Rh, Th
BCC	9.07 ± 0.96	7.74 ± 0.19	Ba, Cr, Fe, K, Li, Na, Nb, Rb, Ta, V, W
HCP	8.51 ± 0.67	5.22 ± 0.23	Be, Cd, Co, Dy, Er, Hf, Mg, Re, Ru, Ti, Tl, Y, Zn, Zr
Binary	8.48 ± 0.34	7.34 ± 0.91	AlTi, Al₃Ti, AlTi₃, AuCu, Au₃Cu, AuCu₃
Combined	8.74	6.19	

Table 1.
Summary table of normalization constants (η^* and λ^*) for four different groups of metals. The two constants for the entire group as combined are shown as combined normalization constants.
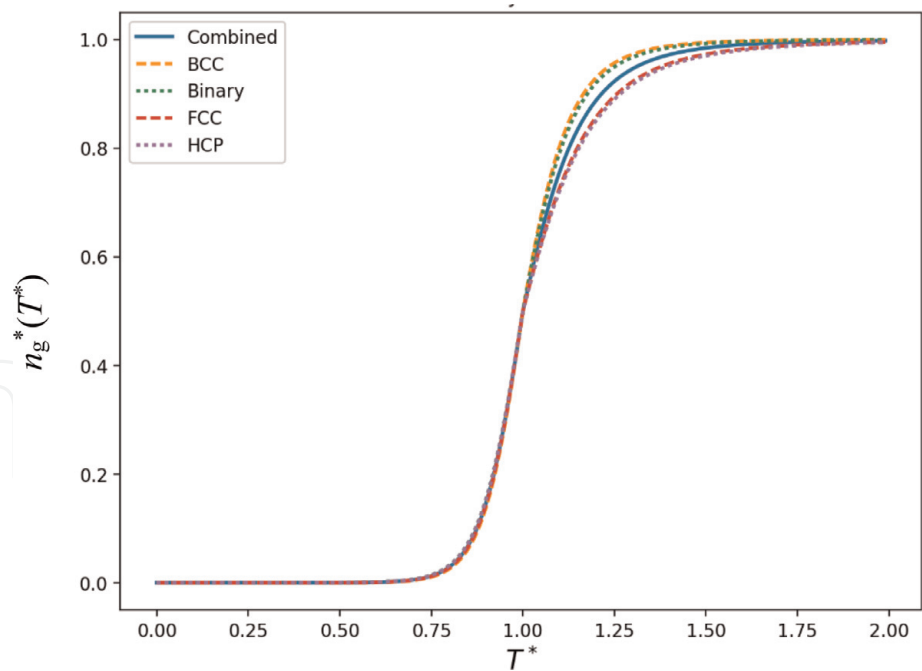
Figure 3.
Normalized best-fit plot of the computed glassy atom density as a function of temperature. The computed glassy atom density versus temperature plots for the alloys in the four different groups are rescaled into one combined fit (solid line). The four subgroup plots are shown individually, according to the legend within the figure. They appear evenly spread out on the two sides of the combined fit solid-line plot.

$$n_g^*(T) = \frac{1}{2} + \frac{1}{2} tanh[s^*(T^* - 1)] \qquad (3)$$

where

$$s^* = \begin{cases} \eta^*, & T^* < 1 \\ \lambda^*/T^*, & T^* \geq 1 \end{cases} \qquad (4)$$

The fitting parameters η^* and λ^* for the four groups of metals are tabulated together with their combined average values in **Table 1**. The list of metals in each individual crystalline symmetry group is given (**Figure 3**).

4. Effect of nanocrystallite size distribution on thermophysical properties

4.1 Annealing and thermal forcing

The dissociation potential of an atom on the surface of a nanocrystallite represents the energy needed to displace the atom to infinity and is of the order of several electron volts, depending on nanocrystallite size and alloy elements. On the other hand, rapid quenching involved in alloy-making leaves many constituent atoms small distances away from their local equilibria, fractions of an electron volt away in energy. This is where thermal forcing differs from annealing in the temperature scale.

Atomic transport is very slow in a metallic alloy medium compared with gaseous media even at elevated temperatures. Consequently, defects in the medium require long relaxation times. The computed number density of glassy atoms at elevated temperatures can be realized only when heating is sustained for very long times. Our laboratory experiments show that thermal forcing requires sustained heating of alloy specimens often for upward to 15 h at each temperature to fully realize the
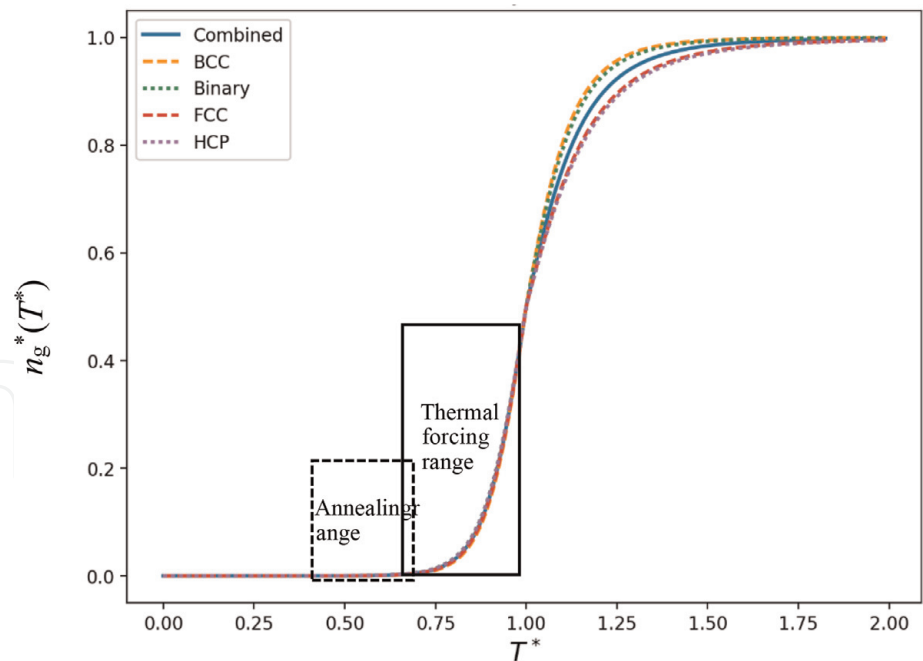
Figure 4.
Annealing and thermal forcing regimes of disordered alloys.

changes in the size distribution function of nanocrystallites. **Figure 4** shows two distinct opportunities for effecting significant changes in the transport properties of metallic alloy specimens.

4.2 Linear thermal expansion coefficient

Theory predicts decrease of the size of nanocrystallites and their number densities with increasing temperature. The temperature dependence of specimen's thermal expansion coefficient $\alpha(T)$ of a disordered alloy specimen would show a nonlinear scaling due to the change in the size distribution of nanocrystallites:

$$\alpha(T) = \gamma(T)\alpha_c(T) + [1 - \gamma(T)]\alpha_g(T) \tag{5}$$

Here $\gamma(T)$ denotes the degree of crystallinity, the probability that an atom is part of nanocrystallites within the specimen at temperature T. $\alpha_c(T)$ is the linear thermal expansion coefficient of the alloy in crystalline form, whereas $\alpha_g(T)$ signifies the linear thermal expansion coefficient of the alloy in fully glassy form. The expansion coefficient of the disordered specimen becomes nonlinear in its temperature dependence because of two different physics at play: one, the disordered specimen is an admixture of two materials that are compositionally identical but structurally different with different mass densities, and different thermal expansion properties; and two, the degree of crystallinity of the specimen, i.e., the fraction of the crystalline part of the specimen, changes when the specimen is thermally forced [6, 7]. **Figure 5** shows the degree of crystallinity computed for $AuCu_3$ as a function of temperature.

4.3 Speed of sound

The general trend of the changes in transport properties, when the specimen's degree of crystallinity is changed under thermal forcing, has been clearly demonstrated in an experiment on sound speed [7]. The measurement with a fresh specimen at room temperature gives the time of sound propagation over the specimen length of 38.2 mm at 90.2 ± 0.9 ms. After the thermal forcing run at 940 K for
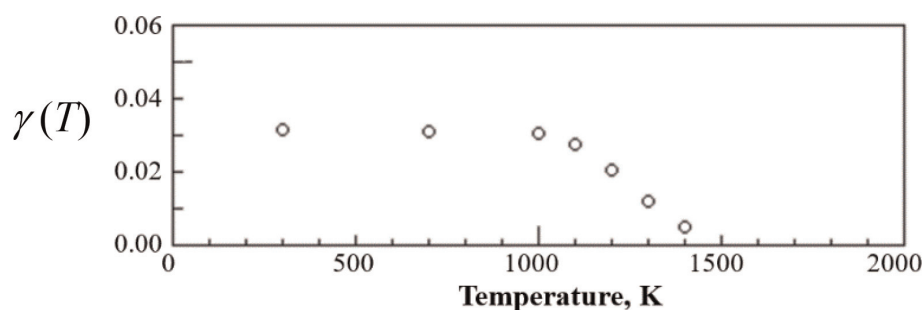
Figure 5.
The degree of crystallinity versus temperature for AuCu$_3$.

16.45 h and quenched in water, the corresponding time of sound propagation at room temperature is found to be 66.5 ± 1.8 ms. The thermal forcing run at 940 K is clearly a case of alloy annealing. For the specimen of 55×45 W% copper-nickel alloy, the melting point is 1543 K, which puts the forcing temperature of 940 K at 60.9% of the melting point. **Figure 4** shows the temperature to be in the alloy annealing regime; the temperature is not high enough to cause dissociation of nanocrystallites and affect their population significantly. The result above shows that the effect of thermal annealing on sound propagation is quite strong. It is in a way not surprising because sound propagation entails small movement of lattice spacing and annealing has nudged atoms within the specimen into positions of deeper binding energies that can be accessed within the thermal energy budget of the order of $k_B T$, or of the order of 0.1 eV. The dissociation potential for removal of an atom from the surface of a nanocrystallite is several eV.

4.4 Diffusion and thermal conduction

The temperature driven changes in the degree of crystallinity forces other thermophysical properties of the alloy specimen to undergo changes also. The temperature dependence of the transport properties, such as thermal conductivity, viscoelasticity, thermal expansion, electrical conductivity and many others, may be estimated approximately by treating the material specimen as a mixture of crystalline and glassy parts whose mixing ratio is variable as a function of temperature after a sustained heating. It is reasonable, however, to anticipate that the estimate may require a higher order correction when the forcing is further intensified.

Quantitative modeling of the temperature dependence of the alloy's transport properties may be addressed in a number of different ways:

i. An alloy specimen may be treated as two slabs of different lattice constants joined linearly. This approach may require appropriate modeling of the issues associated with transmission of excitations at the interface between the two slabs.

ii. Formal analyses may require separate considerations of phonon modes in nanocrystallites versus in the glassy medium. Additional issues of interest may include the structure of the atom pair distribution function and the distribution of coordination numbers.

iii. Computation of the transport properties by the method of Monte-Carlo simulation may entail sending off of random walkers at a given flux at one end of the alloy specimen. Meandering of the walkers and their arrivals at the other end through the medium of glassy matter and nanocrystallites can be tabulated. The alloy medium would be composed of a sampling of glassy

atoms and of nanocrystallites, according to the solution of the system of the law of mass action equations. The Monte-Carlo computation is carried out repetitively at a given temperature in order to develop a sufficiently large ensemble of events.

The size distribution of nanocrystallites evolves under thermal forcing as a function of temperature, and they affect the transport of excitations. In addition, scattering and transmission of random walkers at interfaces of glass-nanocrystallite and nanocrystallite-glass are also likely to play rate-controlling roles.

iv. Alloy specimen may be viewed as a network of interconnections (edges) between atoms. Edges between nanocrystallites are treated as linkages whose resistance to transport of excitation would be governed by the properties of the glassy medium as conduits. Differently from the Internet that carries information without delay or attenuation, the edges would bear the effects of time delays, signal attenuation and transmission speed. Nanocrystallites with multiple degrees (the number of edges) act as relay stations with delay constants that stem from the size of nanocrystallites and branching of the transmission of excitation. While many details of excitation transmission through nanocrystallites have to be worked out, the method holds promise as one with greatest potential [9].

5. Concluding remarks

Disordered metallic alloys have been modeled as a randomly close packed medium of glassy atoms and nanocrystallites of varying size. The model has been implemented by means of a large set of coupled algebraic equations, derived from the law of mass action relations in thermal equilibrium. The size distribution function of the nanocrystallites has been measured from a simulated alloy model in two-dimensions. The size distribution function has been found to depend on the alloy composition. The large system of dissociation equations is solved numerically for the population of constituent species as a function of temperature for 44 different metallic specimens. The theory predicts the degree of crystallinity changing for these alloys as a function of temperature. The melting point is found quite naturally in this alloy model calculations within 5–10% of known values.

It shows that the alloy's thermophysical properties can be changed by changing the size distribution of nanocrystallites. Sustained exposure to thermal forcing can exactly effect the change. By extension, the change of the nanocrystallite size distribution can be affected by means of chemical, mechanical stress or nuclear forcing at sustained elevated temperatures as well. We have shown that the change in the nanocrystallite size distribution function can be predicted by the first-principle model of structurally disordered alloys.

The modeling approach is based on the first-principle method of statistical physics. The model can be further refined and customized for any disordered metallic specimen. The model provides a roadmap for annealing and thermal forcing of disordered alloys. The interesting question is what mechanisms are responsible for the formation of nanocrystallites in metallic solids in the first place. Our continued investigation with the simulated alloy in two-dimensions strongly suggests that the structural disorder in metallic solids appear to originate from vortex-like flow patterns in liquid phase; at phase transition the flow patterns are solidified into disordered structures without recourse for relaxation due to specimen-wide slowing of dynamical processes [9, 10].

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