The Art and Science of Microstructural Control

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A historical perspective on the development of physical metallurgy is presented. Two recent advances in the control of microstructure, rapid solidification and artificial multilayers, are discussed. Rapid solidification has produced metallic glasses and metastable crystalline systems, and has led to important technological and scientific discoveries. The synthesis of artificial multilayers by direct deposition represents the ultimate control of such microstructures.

THE MICROSTRUCTURE OF A MATERIAL IS DETERMINED BY the nature, perfection, and spatial distribution of its constituent phases. These phases can be thermodynamically stable, such as the crystals in a slowly cooled alloy; they can be metastable (that is, stable against small compositional or structural fluctuations but of greater free energy than the corresponding stable phase or phases), such as some supersaturated solid solutions or nonequilibrium compounds; or they can be unstable, such as glasses or spinodally decomposing solutions. The imperfections can be compositional, such as inhomogeneities from solute redistribution during solidification, or structural, such as dislocations or point defects. A description of the spatial distribution of the phases includes size, morphology (dendritic, for example, resulting from the instability of the crystal-melt interface during solidification), connectivity (such as precipitates in a matrix, or alternating lamellae in a eutectic alloy), relative orientation (texture), and the nature of the resulting interfaces (coherent or incoherent).

Historically, metallurgists have been the most successful practitioners of the art of microstructural control to obtain desirable material properties. The early blacksmiths, for example, knew that iron could be hardened by bringing it to a red heat and then quenching it in water; later scientific work showed that this procedure led to the formation of a hard metastable phase known as martensite. The Japanese swordmakers masterfully combined hard carbide and ductile iron phases into a fine composite that was both tough and hard. Application of the methods of modern physics and chemistry to identify and understand the factors that govern the formation of microstructures led to the emergence of a "science of materials," or "physical metallurgy" when applied to metallic systems. As a result, microstructural control has become less a pure art and more a matter of "enlightened empiricism," in which the findings of materials science are used as guidelines for intelligent experimentation. For example, it was found empirically near the turn of the century that aluminum that contained a small amount of magnesium became harder over time. Small-angle x-ray scattering and transmission electron microscopy later showed that this "age-hardening" phenomenon was associated with the formation of very small precipitates that were metastable and coherent. The development of dislocation theory explained how these precipitates increased the resistance to plastic flow. These insights have been used to design new hardenable alloys and to optimize heat treatments.

The first part of this article is a brief historical sketch of the important developments in physical metallurgy from 1940 to 1960. Some of the major advances in microstructural control since 1960 have resulted from the development of techniques for preparing materials that are farther from equilibrium than was previously possible. Two of these techniques will be discussed: rapid solidification and the synthesis of artificial multilayers.

Historical Perspective

The 1940s and 1950s were the golden age of physical metallurgy. These decades saw the development of a remarkable number of important concepts that have had great influence not only on the rest of materials science but also on the physics and chemistry of condensed matter in general. Perhaps the most influential concept has been that of the dislocation, which is a line defect in the crystal lattice. Although the idea of the crystal dislocation was introduced in the 1930s to explain the ease of the plastic deformation in metals, it became fully accepted as a result of experimental work on crystal growth spirals that tested Frank's proposal (*1*) of the screw dislocation mechanism to account for growth at low supersaturation, and of direct observations of dislocation geometry and motion, primarily by transmission electron microscopy on thin metallic foils (*2*). The concept of dislocations was then successfully exploited to explain a variety of mechanical behavior, such as work-, solution-, or precipitation-hardening.

During this period the basic understanding of the kinetics of phase transformations in condensed systems became established. Turnbull and co-workers adapted classical nucleation theory (formulated first by Gibbs and developed in the 1930s by Volmer and others for condensation) to crystallization and solid-state transformations and tested this theory quantitatively (*3*). The origin of the instability of the crystal-melt interface that leads to the formation of dendrites during solidification was identified by Chalmers and co-workers as the constitutional undercooling that resulted from the depression of the liquidus temperature near the interface by rejection of solute from the crystal (*4*); a rigorous mathematical treatment was later given by Mullins and Sekerka (*5*). The phenomenon of spinodal decomposition of quenched solid solutions, that is, the development of phase separation by the unstable growth of composition fluctuations throughout the volume of material, was experimentally established and described quantitatively by the Cahn-Hilliard theory (*6*).

The study of lattice defects other than dislocations also led to major insights: the nature of point defects and their relation to atomic diffusion, short-circuit diffusion along dislocations and grain boundaries, the structure of low- and high-angle grain boundaries, and the kinetics of grain boundary motion.

There are many reasons why physical metallurgy flourished in the

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postwar years. The economic dominance of metals among materials at that time obviously played an important role, as did the emergence of new applications. The development of nuclear technology, for example, spurred the work on lattice defects. It should also be recognized, however, that metals were intrinsically well suited for new scientific investigation: they could be prepared most easily and reproducibly into well-characterized samples; the great number of metallic elements and their alloys provided a wealth of phase transformations for study; the simplicity of the crystal structure of the elemental metals, combined with their ductility, made them prime candidates for the study of lattice defects; and they made excellent samples for the powerful techniques of structural analysis that were emerging, particularly electron microscopy.

Rapid Solidification

Formation of metastable structures. Rapid solidification is one of a number of techniques developed over the last decades that have made it possible to produce metastable (or unstable) microstructures with a higher free energy than was possible before. For example, the presence of internal surfaces, with surface tension γ, at an average spacing r contributes an additional free energy per atom $\Delta f = \gamma\, \Omega/r$, where Ω is the atomic volume, to the total free energy of the system; with these new techniques, it is possible to reduce r to the nanometer scale, which corresponds to values of Δf from 10 to 50 meV per atom. Similarly, the presence of dislocations with a density ρ contributes to $\Delta f = \rho\, \mu\, \Omega^{5/3}/2$, where μ is the shear modulus; extreme cold working (*7*), especially in the presence of hard second-phase particles, can yield dislocation densities as high as 10^{13} cm^{-2}, which also corresponds to Δf values from 10 to 50 meV per atom. Highly supersaturated solid solutions can be formed that have (positive) heats of mixing that correspond to a value of Δf on the order of 100 meV per atom. Many new amorphous solids have been obtained whose excess free energy can be estimated by $\Delta f = \Delta S_f(T_m - T_g)$ [where ΔS_f is the entropy of fusion; T_g is the glass transition (configurational freezing) temperature; and T_m is the melting temperature], which is about 50 meV per atom for metals.

Metastable or unstable structures are formed (*8*) by raising the free energy of the starting materials, for example, by heating (to form the vapor or liquid state), by bombarding with energetic particles (as in sputtering or ion implantation), or by heavy deformation (as in mechanical alloying). The system then has a number of lower free-energy states available into which it can transform upon removal of energy ("quenching"). The actual selection of the final metastable state depends on kinetic factors, such as the quenching rate, the likelihood of nucleation, and the mobility of the phase boundaries. Under certain conditions, no transformation occurs and the frozen state of the high-energy system is obtained, as in glass formation or cold working. For the system to stay in a particular metastable state, it must be quenched to a temperature such that the atomic mobility is sufficiently low to prevent further transformation (configurational freezing).

For some of these quenching processes a cooling rate can be estimated (*9*). In condensation, as in vapor deposition or sputtering, the cooling rate depends on the rate of thermalization of the atoms on the solid surface and is estimated to be 10^{12} K sec^{-1}. A similar estimate is used for the de-energization of atoms after ion bombardment. In rapid solidification, the cooling rate T_t is mainly a function of the smallest dimension of the sample d and the medium used to remove the heat. In melt spinning, the most widely used technique, ribbons that have a thickness of a few tens of micrometers are produced by directing a jet of molten metal onto a cold rotating substrate, which gives a cooling rate of about 10^6 K sec^{-1}. The highest liquid-quenching rates are obtained by picosecond-pulsed laser irradiation of a solid surface (*10*) that concentrates the energy deposition in a thin layer and results in the quenching of a molten overlayer about 100 nm thick. The resulting cooling rate, which is estimated from the relation $T_t \propto d^{-2}$, is 10^{12} K sec^{-1}; the corresponding lifetime of the molten layer (T_m/T_t, which in this case is 1 nsec) has also been measured directly with transient reflectivity. One of the earliest techniques was "splat quenching," in which a shock wave atomizes the liquid into very small droplets that are quenched against a cold substrate with a cooling rate of about 10^8 K sec^{-1}. There are also several gas-cooled atomization processes that can rapidly produce large quantities of cooled powders, which are then compacted into massive objects, with methods such as hot isostatic pressing.

Metallic glasses. In the course of a series of investigations on the formation of metastable crystals, Duwez and co-workers discovered that an amorphous metal could be obtained by rapid quenching of the melt (*11*) in a dramatic confirmation of Turnbull and Cohen's prediction that all liquids, including simple ones such as metals, would form glasses upon cooling if crystallization could be avoided (*12*). This prediction was based on their free volume model for atomic transport in simple liquids and on Turnbull's earlier demonstration that metallic liquids could be cooled far below their thermodynamic freezing point (*3*). Subsequent work by Chen and Turnbull (*13*) established that these amorphous metals were true glasses, in that they exhibited the same characteristics of a liquid-glass transition (such as a discontinuity in the specific heat and the coefficient of thermal expansion, and a sharp, continuous rise in viscosity) seen in materials that easily form glasses, such as silicates and certain organic materials.

Since then these metallic glasses have been the subject of numerous fundamental studies that have contributed considerably to the general understanding of glass formation and the nature of the amorphous state. Studies of their structure, for example, provided information that was more precise and detailed than that available from the study of high-temperature liquids. The topological order in these glasses was found to be polytetrahedral (as in the dense random packing of hard spheres) (*14*), which supported Frank's earlier proposal (*15*) of icosahedral short-range order in simple liquids to account for their resistance to crystal nucleation, since the short-range order in crystals is fundamentally different. The polytetrahedral character of the simple glasses was the basis for recent structural models of the amorphous state that are based on perfect tetrahedral packing in curved space (*16*), and has played an important role in the current interest in the relation between the order in the amorphous state and that in the newly discovered icosahedral crystals (*17*).

The earliest quantitative criterion for glass formation (*18*) was based on the analysis of crystal nucleation that stated that glass formation is favored by a large value of T_{rg}, which is equal to the ratio T_g/T_m. This criterion has proven remarkably successful. One immediate broad implication, that alloy compositions that correspond to deep eutectics should most readily form glasses, has been a useful guide to the identification of new glass-forming systems. A remarkable recent success was the recognition that in the $Pd_{40}Ni_{40}P_{20}$ system T_{rg} was sufficiently large to preclude homogeneous crystal nucleation even at cooling rates of less than 1 K sec^{-1}. Large masses of metallic glass (up to several grams) could be produced from the melt after the heterogeneous nucleants were removed by prolonged heating either in vacuum or in a flux (*19*). Until then the only alternative for obtaining metallic glass in bulk had been shock consolidation of ribbons or powders. With the high quenching rates available from picosecond-pulsed laser irradiation, the limits of glass formation could be tested. For example, it was found (*20*) that under these conditions a minimum of 5 atomic percent boron is sufficient for obtaining iron-boron glasses, whereas in melt spinning at least 12 atomic percent is required. Glass formation in laser quenching is governed by the relative rates of heat removal and crystal growth from the substrate. Only if the crystal growth is collision-limited (that is, if the atoms cross the crystal-melt interface at the thermal vibration frequency, as is the case for simple crystal structures) will it be fast enough to occur under picosecond laser quenching conditions (*10*).

The most important current applications of metallic glasses (*21*) are based on their magnetic properties. Because of the absence of crystal anisotropy and of domain wall pinning sites, such as grain boundaries, some metallic glasses, such as the iron-silicon-boron alloys, are very soft ferromagnets and are used for the fabrication of low-loss power transformer cores. Other magnetic applications include magnetic-tape recorder heads, magnetic shielding, and some electronic components. Since the dislocation mechanisms responsible for the ductility of crystalline metals do not operate in amorphous metals, these materials are unusually strong and hard. Their use as structural materials, however, is still limited because they do not work harden, and because they must compete with well-established, inexpensive alternatives. Their strength is still an asset, however, in the prevention of degradation of the magnetic properties as a result of plastic flow during handling, which is a problem with other soft magnetic materials. Because of the flexibility in alloy composition and the absence of lattice defects, metallic glasses could also have unique surface chemical properties. Improved corrosion resistance has been observed and their catalytic properties are being studied by several groups (*21*).

Crystalline metals. Rapid solidification can have several favorable effects on the microstructure of crystalline metals. First, as a result of copious nucleation (heterogeneous, homogeneous, or dynamic) or breakup of dendrite arms, it results in the formation of smaller grains. Since grain boundaries are barriers to dislocation motion, the smaller grains strengthen the material.

Second, motion of the crystal-melt interface at high velocity can lead to the incorporation of more than the equilibrium amount of solute during the solidification of an alloy. Since the undercooling of the melt can be large under these conditions, some of the supersaturation can be accounted for by local equilibrium at the interface. The rapid solidification experiments of Baker and Cahn (*22*) on a system with a retrograde solidus, however, produced supersaturations greater than the maximum equilibrium solubility and established clearly that the interface did not have to be in local equilibrium. They also described the thermodynamic conditions for "solute trapping," that is, the incorporation of solute atoms accompanied by an increase in their chemical potential as a result of the rapid crystallization of the solvent atoms (*23*). This effect becomes increasingly pronounced as the interface velocity exceeds the diffusive speed v_D of the solvent atoms in the liquid, $v_D = D_\ell/\lambda$ (where D_ℓ is the diffusivity in the liquid and λ is the interatomic distance), which is on the order of 10 m sec^{-1}. In the extreme case, for example, in picosecond-pulsed laser quenching, where the interface velocity can be 100 m sec^{-1} or more, the trapping can be complete, that is, the crystal has the same composition as the liquid. Considerable progress has been made recently in both the theoretical understanding of the nonequilibrium crystallization processes in binary alloys and the experimental verification of those theories. Of particular value have been the direct measurements of the crystal-melt interfacial velocity during rapid solidification of silicon (*24*). The large difference in conductivity between the crystal and liquid allows time-resolved measurements of the melt thickness after pulsed laser irradiation. By applying this technique to silicon that contained various dopants, Aziz and co-workers (*25*) determined the trapping rate at various velocities, which allowed them to discriminate between theoretical models.

This extension of the solubility can have several useful effects. First, it results in greater homogeneity of the solidification products. Second, it makes more solute available for the formation of precipitates during later heat treatments; since these precipitates are often very effective barriers to dislocation motion, they increase the strength of the material. Finally, an increase in solution strengthening due to the direct interaction of the dislocations with the dissolved atoms can also be expected. Figure 1 gives an example for rapidly solidified Ni_3Al that contained different amounts of boron (*26*). This material is important for high-temperature applications, as is evident from the increase in yield stress with temperature (Fig. 1). Pure polycrystalline Ni_3Al, however, is brittle at low temperature because of fracture along the grain boundaries. The addition of a small amount of boron that segregates to the boundaries and enhances cohesion makes the material ductile. Rapid solidification of this alloy allows the boron content to be increased while the ductility is retained. The resulting increase in strength (Fig. 1) is attributed to solution hardening and the smaller size of the grains.

The third way of improving the microstructure by rapid solidification is through its effect on the phase morphology. The stability of the crystal-melt interface, and hence dendrite formation, depends strongly on the interface velocity (*27*). For velocities below v_D, the interface becomes increasingly unstable with increasing velocity because of the greater concentration of rejected solute in the liquid. At high velocities, however, the interface stability increases with increasing velocity because of the surface energy that is associated with the decreasing scale over which the instability can form by diffusive transport. The stability is further enhanced by reduced solute rejection as a result of trapping.

Rapid solidification also produces a finer and more homogeneous distribution of second-phase particles than does conventional casting. This makes it possible to tailor the distribution so that the particles are optimum obstacles to the motion of dislocations, while at the same time their size is small enough to prevent decohesion at the particle-matrix interface, which would be deleterious to the fracture properties (*28*).

Finally, rapid solidification can lead to the formation of metastable crystalline phases. As explained above, the selection of a particular phase depends on kinetic factors of crystal nucleation and growth and therefore cannot be predicted from thermodynamic data alone. Turnbull has suggested that isotropic and simple (small unit cell) structures are kinetically favored (*29*). An instructive illustration of this rule is provided by a series of recent picosecond-pulsed laser quenching experiments on Nb_3Si system (*30*). At the highest quenching rates ($>10^{12}$ K sec^{-1}) the amorphous phase was formed (isotropic, no unit cell). At a slightly lower quenching rate (10^{12} K sec^{-1}) a disordered face-centered cubic phase was formed (cubic point group, 1 atom per unit cell). Further lowering of the quenching rate to 10^{11} K sec^{-1} with the use of a substrate of slightly lower thermal conductivity produced the ordered Cu_3Au-type $L1_2$ phase (cubic point group, 4 atoms per unit cell). When a salt substrate was used, the quenching rate was lowered to 10^8 K sec^{-1} and a new hexagonal phase (uniaxial point group, 16 atoms per unit cell) was found. Melt spinning at 10^6 K sec^{-1} produces the tetragonal Ti_3P-type structure (uniaxial point group, 32 atoms per unit cell).

Serendipitous discoveries. Most of the rapid solidification research described above could be called "planned," in that its results were broadly anticipated by extrapolation of earlier solidification work. But often some exciting scientific or technological discoveries turn up unexpectedly in the course of such planned work.

One example comes from research on permanent magnets (*31*). It is well known that the microstructure can strongly affect magnetic properties. The presence of barriers to the motion of magnetic domain walls, such as grain boundaries or nonmagnetic second-phase particles, tends to increase the coercive force of a material. For this reason, a number of groups in the United States attempted to use rapid solidification to attain such a microstructure. One approach was to produce the material in the amorphous state and to obtain a fine microcrystalline assembly by subsequently annealing. Experiments were performed on iron-based systems that contained rare earth metals, because earlier work showed that these systems had promising magnetic properties. Boron was added because it was known to facilitate glass formation in transition metal–based alloys. The surprise was that annealing of the glass resulted in the discovery of a new, stable, very hard magnetic compound $Nd_2Fe_{14}B$, which was in many ways superior to the existing permanent magnets. The same result was obtained by direct melt spinning at a properly chosen quenching rate. Since the compound is stable, the permanent magnets can also be obtained by the conventional powder metallurgical alignment process, as was found independently by a Japanese group. In all cases, small grains (20 to 80 nm) are required for optimal properties.

A second example is the discovery of quasi-periodic crystals by Shechtman and his associates (*32*). In the course of a research program on rapid solidification of alloys of aluminum and transition metals, Shechtman discovered a metastable phase that gave a sharp electron diffraction pattern with perfect icosahedral symmetry. This was a paradox, since sharp diffraction peaks were assumed to be characteristic of crystalline periodicity, which is known to preclude fivefold symmetry. In the past, similar observations had been explained by twinning, but Shechtman, after several years of careful checking with convergent beam diffraction and dark-field imaging, demonstrated conclusively that his new material was homogeneous, in that every elementary part of a particular crystal displayed the same icosahedral symmetry. This was later confirmed by high-resolution electron diffraction. Since then these materials have been the object of intensive structural investigation and modeling. The sharpness of the diffraction pattern is now clearly understood to be a result of the quasi-periodicity of the structure, which most simply means that it can be mapped onto a higher dimensional periodic crystal, so that its diffraction peaks can be indexed by a finite set of more than three integers (*33*). In retrospect, it became clear that evidence of these quasi-periodic crystals had existed for some time (such as fivefold dendrites). However, it took the astuteness of Shechtman and his colleagues to recognize it and make it into the most important scientific "spin-off" of rapid solidification processing.

Artificial Multilayers

The most direct control of the microstructure of a material is achieved by direct deposition of very thin (0.5 to 10 nm) alternating layers whose thickness can be controlled precisely. If the structure of the two types of layers is the same, these artificial multilayers are often referred to as "compositionally modulated materials," especially if the composition profile changes gradually rather than abruptly.

Attempts to make artificial multilayers began in the 1930s when a number of investigators unsuccessfully tried to produce artificial x-ray mirrors by alternating the electrodeposition of elemental metals from two baths (*34*). The first artificial x-ray mirror was made by Dumond and Youtz in 1940 by alternating the evaporation of copper and gold. The stability of the mirror at room temperature, however, was limited because of rapid interdiffusion, presumably along the moving grain boundaries of the small crystals that made up each of the layers. The same phenomenon was probably also the cause of the failure of the electrodeposition work.

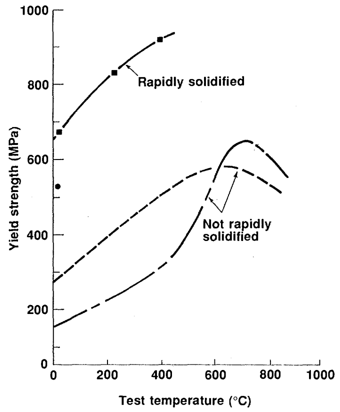

Fig. 1. Yield strength (0.2 percent offset) as a function of temperature for Ni_3Al alloys that contained different amounts of boron. Squares: 1 atomic percent boron; rapidly solidified. Circle: 0.25 atomic percent boron; rapidly solidified. Dashed line: 0.25 atomic percent boron; not rapidly solidified. Dot-dashed line: 0 percent boron; not rapidly solidified. Rapid solidification produces a large increase in strength as a result of grain refinement and solute hardening. [Adapted from (*26*)]

The first stable, well-characterized metallic multilayers were the face-centered cubic compositionally modulated films produced by Hilliard and his associates in the late 1960s (*35*). With the use of an elegant shuttered two-source evaporation technique, they deposited the films on a mica substrate, which gave a strong [111] texture with grain boundaries perpendicular to the plane of the film that were stable against grain growth.

The aim of their work was to test the theory of spinodal decomposition (*6*) directly on artificially created, well-characterized compositional "fluctuations." The crucial element of the Cahn-Hilliard theory is that the free energy F of an alloy system that is inhomogeneous on a very small scale is not simply the sum of the bulk free energies $f(c)$ (of all volume elements dV of composition c) but also contains a term proportional to the square of the composition gradient:

$$F = \int [f(c) + \kappa(\nabla c)^2]\, dV \qquad (1)$$

where κ is the gradient energy coefficient and the integral is over the entire volume of the system. Since this gradient energy also contributes to the driving free energy for diffusion, the interdiffusion coefficient D_λ that governs the evolution of a sinusoidal composition profile becomes dependent on the repeat length λ:

$$D_\lambda = D[1 + 2\kappa(2\pi/\lambda)^2/f''] \qquad (2)$$

where D is the bulk interdiffusion coefficient and f'', which is the second derivative of the free energy with respect to the composition, is obtained from thermodynamic data. D_λ can be determined experimentally from the rate of decay with annealing time of the diffraction satellites that arise from the presence of the composition modulation. From a series of experiments on gold-silver films with different repeat lengths, Cook and Hilliard (*36*) made the first direct measurement of κ. They also found perfect agreement between the extrapolation (over ten orders of magnitude) of the temperature dependence of their bulk interdiffusivity and earlier measurements at high temperature; that the evolution of the composition profile in their samples is governed by the lattice diffusivity and not by short-circuit diffusion is due to the fact that the modulation wavelength is much shorter than the distance between extended defects.

If the lattice parameter a depends on the composition, then coherency stresses will be present in the modulated films that will cause the coherent diffusivity $D_{\lambda,\mathrm{coh}}$ to be greater than the value given by Eq. 2. This was first calculated by Cahn for spinodal decomposition:

$$D_{\lambda,\mathrm{coh}} = D_\lambda + 2M\,\eta^2 Y \qquad (3)$$

where M is the mobility, $\eta = d(\ln a)/dc$, and Y is an elastic modulus.

Philofsky and Hilliard (*37*) indeed observed a decrease in the interdiffusivity in copper-palladium films that corresponds to the loss of coherency with increasing modulation repeat length.

Metallic artificial multilayers can at this time be produced by a variety of deposition methods: evaporation, sputtering, molecular beam epitaxy, and electrodeposition. Multilayers that consist of metals with different crystal structures, of amorphous and crystalline layers, and of fully amorphous modulated films have been produced. Their main technological application has been as artificial x-ray mirrors, which are usually made of materials with very different electron densities, such as polycrystalline tungsten and amorphous carbon (*38*).

Because the compositionally modulated films allow the highest sensitivity for diffusion measurements, they have also been used in the study of diffusion in amorphous metals (*35*), a process that is of necessity slow, since otherwise rapid crystallization occurs. Because these measurements are nondestructive, the technique allows the diffusivity to be monitored as a function of time, which is crucial for measuring the relaxation of an amorphous metal. As shown in Eq. 2, the dependence on the repeat length also allows insight into the thermodynamics of the amorphous alloy system.

The artificial metallic multilayers have several interesting physical properties. The electrical, magnetic, and optical properties of these multilayers should be affected by bringing very dissimilar materials into close contact, as well as by limiting the dimensions of an individual component (*38*). One of the most dramatic effects, however, is the increase by as much as a factor of 4 of the elastic moduli of many compositionally modulated films with repeat lengths of about 2 nm. The theoretical models for this "supermodulus effect" fall in two categories: those based on the interaction of the Fermi surface with the artificial Brillouin-zone boundary created by the modulation, and those based on the higher order elastic effects associated with the coherency strains. None of these theories are quantitatively satisfactory (*39*).

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