Dissolving Equilibrium-Immiscible Elements *via* Severe Plastic Deformation*

E. Ma

Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218, USA

Severe plastic deformation has the fascinating power of alloying equilibrium-immiscible elements, overriding the thermodynamic driving force (positive heat of mixing) that would dictate phase separation in equilibrium. This article briefly reviews the current understanding of this subject, in terms of experimental evidence for atomic-level alloying and phase selection, and in particular the models proposed to explain the driven intermixing. Outstanding issues that await future research are also discussed. [doi:10.2320/matertrans.47.1269]

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1. Introduction

There are many couples of simple metals such as Ag and Ni, or Cu and Ta, where the two elements exhibit a positive heat of mixing (positive ΔH).¹⁾ The positive ΔH may arise from a large atomic size mismatch between the two elements, or has chemical origins rooted in their electronic structures. In thermodynamic equilibrium, solid-state alloying between such “immiscible elements” is not possible at ordinary temperatures (*i.e.*, at temperatures not sufficiently high for the entropy term to overwhelm the ΔH). In binary phase diagrams, the two elements would show little or no mutual solid solubility, nor intermetallic compounds.¹⁾ When the two elements are coupled together, the thermodynamic driving force biases the thermal diffusion in the direction of phase separation rather than intermixing.²⁾

During the past decade or so, a number of experiments have demonstrated that many equilibrium-immiscible elements can be made to alloy when the diffusion couples is subjected to severe plastic deformation (SPD) to large strains. In other words, the externally imposed randomizing action forces the issue despite the fact that the two species dislike each other. The typical deformation routes used were ball milling of powder mixtures,^{3–13)} cold rolling of stacked multilayers,¹⁴⁾ extrusion of *in situ* composites,¹⁵⁾ and high pressure torsion.¹⁶⁾ Studies of deformation-driven alloying overcoming thermodynamic driving forces are motivated not only by the science appeal of this fundamental subject, but also by the unusual properties resulting from the nonequilibrium alloys created. In the arena of physical metallurgy, the new alloys present challenges and rich research opportunities for understanding the thermodynamics and kinetics of phase transformations, in particular in driven systems. For applications, the artificially created alloys and their derivative nanocomposites are of interest for a number of physical/chemical properties, including ferromagnetism,¹⁷⁾ giant magnetoresistance,¹⁸⁾ suppressed melting temperature of nanoparticles,¹⁹⁾ novel phase equilibria on surfaces,^{20,21)} superior mechanical strength,²²⁾ self-organized nanoscale patterning,^{23,24)} etc.

The early evidence for alloying between positive H elements was provided by x-ray diffraction (XRD), such as

Fig. 1 Typical X-ray diffraction patterns²⁵⁾ for $\text{Fe}_{50}\text{Cu}_{50}$ powder samples after different ball milling times: (a) 10 h, (b) 30 h, (c) 50 h, and (d) 100 h.

the XRD pattern cited in Fig. 1.²⁵⁾ With increasing ball milling time at room temperature, a two-phase powder mixture (fcc + bcc) of Cu and Fe gradually evolve into a single fcc phase, Fig. 1 (from top to bottom), even though in the equilibrium phase diagram there is virtually no solubility between Cu and Fe at temperatures below about 700°C. As a function of composition, fcc solutions are obtained in Cu-rich mixtures, whereas bcc solutions are produced on the Fe-rich side. In between, for a range of compositions there is a two-phase coexistence region (see below).²⁶⁾ For systems such as Ag-Cu, continuous fcc solid solutions were obtained across the entire composition range,²⁷⁾ with possible amorphization of some local regions.¹⁴⁾ All the alloys created, be it fcc, bcc, or amorphous in structure, show heat release upon transformation to ground state (a mixture of the two constituent elements) during annealing in a calorimeter, confirming that deformation-induced alloying is an uphill process creating a new alloy with positive heat of mixing.^{14,27–29)}

Several questions immediately come to mind. Are the two elements, say, Cu and Fe, really alloyed on atomic scale forming random solid solution, or is the product a nanocomposite (mixture of nanoscale fcc and bcc domains so small that they are beyond the resolution of conventional

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Fig. 2 Fourier transforms (FTs) of EXAFS functions of Cu, Fe, $\text{Fe}_{50}\text{Cu}_{50}$, and $\text{Cu}_{20}\text{Fe}_{80}$, showing atomic shells and fcc and bcc signatures. The changes in atomic configurations surrounding the absorbing atom before and after ball milling are clearly revealed. For ball milled $\text{Fe}_{80}\text{Cu}_{20}$, the Cu K edge FT no longer matches that of pure Cu but instead bears a bcc signature, similar to that in the Fe K edge data from the same sample. This provides direct evidence that the Cu atoms in $\text{Fe}_{80}\text{Cu}_{20}$ are now incorporated into bcc coordination. For milled $\text{Fe}_{50}\text{Cu}_{50}$, the FTs at not only the Cu edge, but also the Fe edge closely resemble the fcc signal of pure Cu, suggesting fcc coordination surrounding both Cu and Fe. These bcc and fcc signatures are evident out to 0.6 nm, containing peaks up to the fifth neighbor. The structures found are consistent with X-ray diffraction and TEM results for similar alloys, but the EXAFS data more clearly demonstrate a well-developed bcc coordination of Cu atoms in $\text{Fe}_{80}\text{Cu}_{20}$ and fcc coordination of Fe atoms in $\text{Fe}_{50}\text{Cu}_{50}$. Quantitative fitting results have been reported in Ref. 30.

characterization techniques)? What determines the observed phase selection (fcc versus bcc, and in competition with amorphization)? Why and how are Cu and Fe mixed during deformation? These issues have been addressed in the literature, as discussed briefly in the following sections of this overview. More discussions on the atomic-level chemical mixing and structure, as well as phase selection and competition, can be found in Ref. 29). This article focus more on a summary of the explanations and alloying mechanisms discussed in the literature. A main objective of this overview is to stimulate interest and encourage activities in this area; to this end we will also outline some unresolved issues that should be addressed with in-depth research.

2. Atomic-Level Alloying, Phase Competition and Selection

The main characterization routes used to prove atomic-

Fig. 3 Through linear combination fitting of a XANES spectrum, the fractions of fcc and bcc phases in the two-phase mixture can be determined. In this case the Cu K edge XANES spectrum of $\text{Fe}_{67.5}\text{Cu}_{32.5}$ is simulated as a linear combination of 0.57 times the Cu K edge spectrum of $\text{Fe}_{80}\text{Cu}_{20}$ (bcc component) and 0.43 times the Cu K edge spectrum of $\text{Fe}_{50}\text{Cu}_{50}$ (fcc component).

level alloying are magnetic property measurements (see a review in Ref. 25), x-ray absorption fine structure studies³⁰⁾ (Extended x-ray absorption fine structure, or EXAFS, and X-ray absorption near edge structure, XANES²⁶⁾), and 3D atom probe characterizations.^{16,31)} The EXAFS results for Fe–Cu³⁰⁾ are shown in Fig. 2. In addition to proving the fcc and the bcc structures, the phase fractions and phase compositions in the two-phase co-existence region can also be identified simultaneously using XANES.^{26,32)} Fig. 3. The results suggest overlapping solubility rather than lever rule, as described in Fig. 4. In other words, the system has been driven to undergo homogeneous chemical intermixing, across the entire composition range. A review of these features can be found in Ref. 29).

More recently, atom probe work has provided nanometer scale information regarding the interdiffusion of Ag–Cu and Fe–Cu systems after SPD processing. A filamentary composite refined by cold drawing was processed by high pressure torsion (HPT).¹⁶⁾ The nanostructured Fe resulting from this SPD processing dissolved in the Cu matrix, forming Cu-based supersaturated solid solutions contain up to 20 at% Fe. The composition profile obtained using the 3D atom probe is shown in Fig. 5. The authors analyzed the interdiffusion kinetics in terms of a dramatic increase of the vacancy concentration during SPD. K. Hono *et al.* further exploited the powerful 3D atom probe technique, for composition profiling in wire-drawn Cu–Ag.³¹⁾ Their most recent results are yet to be published.

3. Mechanisms of Driven Alloying and Uphill Interdiffusion

As mentioned above, this article attempts to present, for the most part, an overview of the current understanding of the mechanisms. Why would SPD be able to overcome the positive ΔH to alloy the two elements is obviously an interesting question. The early attempts at explaining the intermixing observed started with simple thermodynamic

Fig. 4 Compositions of the bcc and fcc phases in the two-phase region of ball-milled Fe–Cu alloys. The solubilities are not just extended to the near-end limit of the two-phase region, as dictated by the lever rule for the conventional two-phase coexistence in thermodynamic equilibrium, but that the two-phase region represents a complete overlap of solubility for the two phases (fcc and bcc solutions).

arguments. Free energy versus composition curves were calculated to rationalize the cross-over from fcc solution to bcc solution in the Cu–Fe system.^{5,8,9,26)} Such explanations, while helpful in rationalizing phase selection, do not provide an atomistic mechanism as to how the two elements in the diffusion couple, as depicted in Fig. 6(a), are intermixed. In other words, exactly how interfacial mixing commences and proceeds remains mysterious, when the two slabs of A and B are coupled together as shown in Fig. 6(b). Several authors have considered possible sources of additional thermodynamic driving forces that can lead to interdiffusion. For example, Gente *et al.*¹⁰⁾ proposed that during SPD, grain sizes (or the thickness of individual elemental layers) are continuously refined down to the 10 nm range, and coherent (or semi-coherent) domains below 10 nm are formed. The newly generated interfaces provide excess interfacial energy that destabilizes the layered structure and favors random alloys. However, to generate the thermodynamic driving force required such that diffusion turns downhill rather than uphill, the layers would have to be refined down to below about 1 nm.²⁾ This is inconsistent

Fig. 6 (a) A schematic showing a diffusion couple composed of a slab of A atoms (block on the left) butted to a slab of B atoms (block on the right), (b) A schematic showing the intermixing at the interface between A and B slabs. The intermixed interfacial layer composed of both A and B atoms are shown in the lower panel. (Courtesy of T. Z. Luo)

with experimental observations that alloying occurs in domains at least a few nanometers in size.^{10,33)}

A related mechanism was proposed by Yavari *et al.*^{6,11)} Instead of layered planar structures, they invoke curvature effects in extremely small particles. The chemical potential is raised by the Gibbs–Thomson term due to their small radius

Fig. 5 3D atom probe data set of the Cu–Fe composite after five HPT turns (a) 3D reconstructed volume ($3 \times 3 \times 12 \text{ nm}^3$), only Cu atoms are displayed to exhibit nanoscaled Cu and Fe grains; (b) Cu concentration profile across Cu/Fe interfaces, showing obvious intermixing.¹⁵⁾

of curvature and surface energy. In other words, there is a capillary pressure at sharp tips that dissolves atoms into the matrix. The required radius of curvature is of the order of 1 nm. Such a scenario may exist for the sharp tip of filaments. But it is not clear how often sharp tips are created during SPD. Also, instead of dissolving the tip atoms into the matrix through bulk diffusion, there is now also a driving force for the tip atoms to migrate to other regions of the filament with larger radius of curvature *via* fast interface diffusion.²⁾ For small particles and relatively low temperature, a simple dimensional analysis indicates that the time constant for the latter process is actually smaller than that for dissolution into the matrix through bulk lattice diffusion.³⁴⁾ Due to this kinetic advantage, a filament with sharp tips would sphereodize rather than dissolve, as observed in many experiments.

Schwarz³⁵⁾ (and Eckert *et al.*,^{3,4,7)} to some extent) has suggested mechanisms based on interactions between the dislocation strain fields and the solutes. They hypothesized preferential segregation of solute atoms into core regions of dislocations, which are abundant in SPD materials. Diffusion in this core region is fast enough for solutes to enter in large quantities during SPD.³⁶⁾ When dislocations move away, some solutes are left behind, resulting in supersaturated solid solutions. While this mechanism seems to be plausible in some systems,^{35,36)} it seems doubtful if the mechanism can be sufficiently effective when the two elements have similar sizes (such as Cu–Fe, Co–Cu) and therefore not much tendency for the solute to diffuse to or segregate to dislocation core regions. It would be hard pressed to rationalize the formation of a highly concentrated solution enriched in the solute. Large scale MD simulation is required to better understand this mechanism.

Kinetic models based on “ballistic” mixing have also been proposed. Bellon and Averbach³⁷⁾ describe the alloying process as a competition between sustained external forcing (*e.g.* due to shearing of atomic planes during plastic deformation) and decomposition due to thermal diffusion. The steady state the system reaches is determined by the rate balance of forced mixing events and decomposition events. The same mechanism of phase transformation in a ‘driven system’ has also been applied previously to the order-disorder transitions of intermetallics under milling³⁸⁾ or irradiation,³⁹⁾ originally proposed by G. Martin’s group. The driven mixing was described as due to shuffling of atomic planes, much like shuffling of a deck of cards.

Most recently, Odunuga *et al.*⁴⁰⁾ advanced this idea, by performing molecular dynamics simulations of forced atomic mixing in crystalline binary alloys during plastic deformation at 100 K. Configurations were created, with a *B* precipitate (a sphere 4.0 nm in diameter) in an *A* matrix (32,000 sites on a face centered cubic lattice, thus of edge length of 7.3 nm, and cube edges along the (100) directions). Compressive strains were cyclically applied along the normals of the simulation cell faces by scaling atomic positions at a constant strain rate of $5 \times 10^9 \text{ s}^{-1}$. Each compression lasted 48 ps, thus producing an average strain of 24%. The amount of mixing was monitored by performing a nearest neighbor analysis and then calculating the chemical short-range order (CSRO) parameter, Ω . This CSRO parameter takes values of -1.0 , 0.0 , and 1.0 for microstructures that are fully decomposed,

Fig. 7 Evolution of the chemical short-range order parameter Ω for several model alloy systems (see Ref. 40 for details). Most of these MD simulation runs resulted in a completely mixed random solution with Ω approaching zero.

random, or fully ordered, respectively. Figure 7 summarizes the evolution of the CSRO parameters for selected runs. The first observation is that for most runs (see Ref. 40 for details) the Ω value tends to zero, *i.e.*, nearly complete atomic mixing.

In order to visualize how mixing proceeds, the authors identified all nearest neighbor pairs of atoms at a certain time, and then recalculated the separation distance of these pairs at later times.⁴⁰⁾ In the histogram of the change of separation distances, they found peaks centered at values corresponding to the modulus of the Burgers vectors of partial dislocations and perfect dislocations, respectively. In other words, such MD simulations illustrate that it is the slip mediated by dislocations that mixes the constituent elements, disregarding the magnitude of positive heat of mixing. Interestingly, in an analysis of the displacement field, in particular the separation versus time, the authors found that the dislocation glide induced mixing resembles the forced mixing of a substance advected by a turbulent flow. More details discussing this analogy between the SPD-driven mixing and the turbulent convective flow are expected to come out from these authors’ group in their future publications.

Our group constructed a phenomenological model as a simple way to rationalize the large solubility observed.^{2,41,42)} This model analyzes solubility extension by incorporating both the thermodynamic and dynamic effects without a full, quantitative knowledge of the relative contribution of each individual mechanism.⁴²⁾ The formula starts from the textbook solubility equation that predicts equilibrium solubility. In a non-equilibrium, externally driven system, it is not appropriate to determine solubility using an equation derived from simple chemical potential considerations. However, for the sake of observing the overall equivalent effects, in our model the kinetic forcing effects have been artificially converted into effective changes in free energy and chemical

potential in the system following Martin's approach. As such we can summarize, using a new solubility equation, several mechanisms proposed for SPD induced alloying, including the mutually enhancing effects of chemical driving force changes in the SPD material (*i.e.*, reduced driving for demixing in a nanostructure with high defect content), and the kinetic driven intermixing brought in by the mechanical deformation. The total atomic flux is now driven by an effective free energy, which, when compared with conventional free energy, has an apparent enhanced entropy or alternatively an elevated effective temperature.^{41,42)} The ballistic events that drive randomization mix pump excess entropy into the system. Alternatively, one can also estimate the effective spinodal temperature, which is now significantly lower than the thermodynamic spinodal temperature due to the elevated entropy term. The miscibility gap is therefore closed at a relatively temperature.⁴¹⁾

We could view the interfacial mixing depicted in Fig. 6(b) from yet another perspective, as a consequence of stress-biased, thermally activated motion of atoms. Consider the rate equations for the stress-biased atomic movements at the interface (Figs. 6(a) and 6(b)), where the free energy difference, for an A atom that enters the B side, is Δg (which is positive and discourages mixing). The forward jump rate along the stress direction is

$$K_f = v_0 \exp\left(-\frac{\Delta F - \tau V + \Delta g}{kT}\right).$$

Here v_0 is the attempt frequency of atomic jumps, ΔF is the energy barrier, or the Helmholtz free energy of activation, for an A atom to move into the B slab (Fig. 6(b)), τ is the applied shear stress, V is atomic volume (or molar volume), k is Boltzmann constant, and T is temperature. The energy barrier is reduced by the work done by the applied stress, τV . The backward jump rate is

$$K_b = v_0 \exp\left(-\frac{\Delta F + \tau V}{kT}\right)$$

The net jump rate K is given by $K = K_f - K_b$,

$$K = v_0 \exp\left(-\frac{\Delta F}{kT}\right) \left\{ \exp\left(-\frac{\Delta g - \tau V}{kT}\right) - \exp\left(-\frac{\tau V}{kT}\right) \right\}$$

When the stress term is absent, obviously

$$K = v_0 \exp\left(-\frac{\Delta F}{kT}\right) \left\{ \exp\left(-\frac{\Delta g}{kT}\right) - 1 \right\}$$

Since Δg is positive, K is negative such that there is no diffusion. For interdiffusion to occur, we need

$$2\tau V > \Delta g$$

$$\exp\left(-\frac{\Delta g - \tau V}{kT}\right) - \exp\left(-\frac{\tau V}{kT}\right) > 0.$$

For $\Delta g = 10$ kJ/mol and $V = 10$ cm³/mol, we need

$$\tau > 500 \text{ MPa}.$$

This shear stress level is easily reached in SPD, where the eventual nanostructures developed *via* SPD often deform at such high stresses. But if we want to mix a liquid-immiscible system with a large $\Delta g > +30$ kJ/mol,⁴¹⁾ then we need $\tau = 1.5$ GPa (or normal stress of the order of 3 GPa). Such a shear

stress level may not be achievable (except perhaps at occasional local stress concentrations), especially when one of the metals is relatively soft (low in strength).

The next question is, can we get enough interdiffusion for observation of intermixing in experiments? The diffusivity can be estimated as

$$D = v_0 a^2 C_v \exp\left(-\frac{\Delta G}{kT}\right) = v_0 a^2 C_v \exp\left(-\frac{\Delta F - \tau V}{kT}\right).$$

Using $v_0 = 10^{13}$ /s, $a = 0.2$ nm, $T = 400$ K, $C_v \sim 0.001$ during deformation (the instantaneous vacancy concentration could be as high as 0.1% before recovery takes away a major portion⁴³⁾), $\tau = 1$ GPa, $\Delta F = 0.5$ eV, $t = 1$ sec, the diffusion distance in a typical metal would then be roughly

$$x = \sqrt{4Dt} = 50 \text{ nm}.$$

This is of course a crude analysis that should not be taken literally as a prediction of interdiffusion distance. But it at least suggests that the magnitude of penetration can be easily detected in composition profiling experiments such as those in Fig. 5.

4. Summary and Remaining Issues

A main purpose of this overview is to call to the attention of the SPD community that heavy plastic deformation, in addition to its well-studied capabilities (to refine grain sizes,⁴⁴⁾ consolidate powders, and induced phase transformations such as amorphization), can also lead to the mutual dissolution of elements with positive heat of mixing. This is an interesting experimental observation by itself, and raises challenges to the understanding of interdiffusion in an externally imposed field (in our case, stresses). Unresolved issues abound, with rich research opportunities. First, the alloyed phases thus far are mostly supersaturated crystalline solid solutions. Occasionally there have been reports of amorphous alloys, but unlike for negative ΔH systems, the amorphization is rare and usually small in scale. It is not fully understood if and when full amorphization can be induced between two equilibrium-immiscible elements *via* SPD.⁴⁵⁾ Second, so far the driven alloying has been demonstrated for several processing routes, including cold rolling, ball milling, high pressure torsion, and extrusion, provided the input plastic strain is sufficiently large. A comparison of these techniques, each possibly having its own features and attributes, has not been carried out. Third, a detailed experimental monitoring of the alloying/interdiffusion process is still lacking, especially for the early stages and for an atomic-level view of the intermixing process. Fourth, there has been no demonstration of alloying in liquid-immiscible elements (systems with large positive heat of mixing), at least not in a convincing manner or on large scales. The proposed reasons⁴⁰⁾ are to be further explored and substantiated. Fifth, a number of models have been put forward to explain the alloying and/or phase selection, but each model only looks at the problem from a specific perspective and has obvious limitations. The models discussed above should be regarded as viewpoints that remain to be critically assessed, rather than fully established mechanisms. Exactly how the atoms are transported at an interface against the thermodynamic driving

force remains largely mysterious. As the nature of the “ballistic” mixing action (assumed to be analogous to the collision recoils in ion irradiated materials³⁹⁾) is only beginning to be unraveled. How the magnitude of the stresses impacts the alloying outcome is unclear. Finally, recent modeling work^{40,46)} has not yet resolved the debate that under what conditions completely homogeneous mixing and “polymorphic constraints”⁴⁷⁾ can be safely assumed. In general, a fully established modeling framework for this problem requires novel concepts and tools.⁴⁰⁾

Clearly, the unique and nonequilibrium process of atomic transport/exchanges under high stresses during plastic deformation, with complex interplay with thermodynamic driving forces, is a fascinating, fundamental science problem. To conclude, it is the opinion of this author that continued experimental and modeling efforts should be devoted to developing a better understanding of the mechanisms underlying the deformation-induced intermixing of equilibrium-immiscible elements. This short overview hopefully serves as a starting point to stimulate renewed interest in this subject, especially as new and more powerful experimental and simulation tools/ideas become available to future researchers.

REFERENCES

- 1) T. B. Massalski (Ed.), *Binary Alloy Phase Diagrams*, vols. 1–3, (ASM, Metals Park, OH, 1986).
- 2) E. Ma, H. W. Sheng, J. H. He and P. S. Schilling: *Mater. Sci. Eng. A* **286** (2000) 48.
- 3) J. Eckert, J. C. Holzer, C. E. Krill III and W. L. Johnson: *J. Appl. Phys.* **73** (1993) 131.
- 4) J. Eckert, J. C. Holzer, C. E. Krill III and W. L. Johnson: *J. Appl. Phys.* **73** (1993) 2794.
- 5) E. Ma, M. Atzmon and F. Pinkerton: *J. Appl. Phys.* **74** (1993) 955.
- 6) O. Drbohlav and A. R. Yavari: *Acta Metall. Mater.* **43** (1995) 1799.
- 7) J. Eckert, J. C. Holzer, C. E. Krill III and W. L. Johnson: *J. Mater. Res.* **7** (1992) 1980.
- 8) B. Fultz, C. C. Ahn, L. B. Hong, *et al.*: *Metall. Mater. Trans.* **27A** (1996) 2934.
- 9) L. B. Hong and B. Fultz: *Acta Mater.* **46** (1998) 2937.
- 10) C. Gente, M. Oehring and R. Bormann: *Phys. Rev. B* **48** (1993) 13244.
- 11) A. R. Yavari, P. J. Desre and T. Benamer: *Phys. Rev. Lett.* **68** (1992) 2235.
- 12) G. Mazzone, V. Rosato, M. Pintore, F. Delogu, P. Demontis and G. B. Suffritti: *Phys. Rev. B* **55** (1997) 837.
- 13) K. Uenish, K. Kobayashi, K. Ishihara and P. H. Shingu: *Mater. Sci. Eng. A* **134** (1991) 1342.
- 14) H. W. Sheng, G. Wilde and E. Ma: *Acta Mater.* **50** (2002) 475.
- 15) X. Sauvage, L. Renaud, B. Deconihout, D. Blavette, D. H. Ping and K. Hono: *Acta Mater.* **49** (2001) 389.
- 16) X. Sauvage, F. Wetscher and P. Pareige: *Acta Mater.* **53** (2005) 2127.
- 17) W. Q. Zhang and E. Ma: *J. Mater. Res.* **15** (2000) 653.
- 18) J. R. Childress and C. L. Chien: *Phys. Rev. B* **43** (1991) 8089.
- 19) H. W. Sheng, K. Lu and E. Ma: *Acta Mater.* **46** (1998) 5195.
- 20) P. T. Sprunger, E. Lagsgaard and F. Bensenbacher: *Phys. Rev. B* **54** (1996) 8163.
- 21) H. W. Sheng and E. Ma: *Phys. Rev. B* **61** (2000) 9979.
- 22) L. He and E. Ma: *Nanostructured Materials* **7** (1996) 327.
- 23) R. A. Enrique, K. Nordlund, R. S. Averback and P. Bellon: *J. Appl. Phys.* **93** (2003) 2917.
- 24) R. A. Enrique and P. Bellon: *Phys. Rev. B* **60** (1999) 14649.
- 25) J. Z. Jiang, C. Gente and R. Bormann: *Mater. Sci. Eng. A* **242** (1998) 268.
- 26) P. J. Schilling, J. H. He, R. C. Tittsworth and E. Ma: *Acta Mater.* **47** (1999) 2525.
- 27) R. Najafabady, D. J. Srolovitz, E. Ma and M. Atzmon: *J. Appl. Phys.* **74** (1993) 3144.
- 28) T. Klassen, U. Herr and R. S. Averback: *Acta Mater.* **45** (1997) 2921.
- 29) E. Ma: *Prog. Mater. Sci.* **50** (2005) 413.
- 30) P. J. Schilling, J. H. He, J. Cheng and E. Ma: *Appl. Phys. Lett.* **68** (1996) 767.
- 31) S. Ohgaki, K. Yamazaki and K. Hono: *Scripta Mater.* **48** (2003) 1569.
- 32) P. S. Schilling, V. Palshin, J. H. He and E. Ma: *Phys. Rev. B* **68** (2003) 224204.
- 33) J. Y. Huang, J. Z. Jiang, H. Yasuda and H. Mori: *Phys. Rev. B* **58** (1998) 11817.
- 34) D. Josell and F. Spaepen: *MRS Bull.* **24** (2) (1999) 39.
- 35) R. B. Schwarz: *Mater. Sci. Forum* **269–272** (1998) 665.
- 36) Y. Estrin and E. Rabkin: *Scripta Mater.* **39** (1998) 1731.
- 37) P. Bellon and R. S. Averback: *Phys. Rev. Lett.* **74** (1995) 1819.
- 38) P. Pochet, E. Tominez, L. Chaffron and G. Martin: *Phys. Rev. B* **52** (1995) 4006.
- 39) G. Martin: *Phys. Rev. B* **30** (1984) 1424.
- 40) S. Odunuga, Y. Li, P. Krasnochtchekov, P. Bellon and R. S. Averback: *Phys. Rev. Lett.* **95** (2005) 045901.
- 41) E. Ma, J.-H. He and P. J. Schilling: *Phys. Rev. B* **55** (1997) 5542.
- 42) E. Ma and M. Atzmon: *Mater. Chem. Phys.* **39** (1995) 249.
- 43) J. Xu, J.-H. He and E. Ma: *Metallurgical Transactions A* **28** (1997) 1569.
- 44) Y. T. Zhu, J. Y. Huang, J. Gubicza, T. Ungar, Y. M. Wang, E. Ma and R. Z. Valiev: *J. Mater. Res.* **18** (2003) 1908.
- 45) E. Ma: *Scripta Mater.* **49** (2003) 941.
- 46) A. C. Lund and C. A. Schuch: *Phys. Rev. Lett.* **91** (2003) 235505.
- 47) E. Ma and M. Atzmon: *Phys. Rev. Lett.* **67** (1991) 1126.