Stability in thin film multilayers and microlaminates: the role of free energy, structure, and orientation at interfaces and grain boundaries

A.C. Lewis [a,*], D. Josell [b], T.P. Weihs [a]

[a] *Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218, USA*
[b] *Metallurgy Division, NIST, Gaithersburg, MD, USA*

Abstract

In polycrystalline multilayer systems, the free energies of the interfaces and grain boundaries will determine the relative stability of each layer as well as the overall stability of the system. The stability of immiscible systems and systems that form intermetallic compounds is discussed, and the effects of texture and orientation of grains on stability are examined.
© 2003 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Stability; Laminates; Grain boundary energy; Interfacial free energy; Multilayers

1. Introduction

Layered structures are found in a number of applications ranging from magnetic to structural, and the stability of the individual layers is often critical to the performance of the material. For example, metal/intermetallic multilayers are being considered as thin outer walls for jet turbine blades with advanced cooling designs [1–4]. For the multilayers to be structurally sound under the operating conditions, the individual layers in the laminates must be stable under severe thermal and mechanical loads. Stable layered microstructures are also very important in many low- to moderate-temperature applications. Multilayer sensors in magnetic storage, copper lines in integrated circuits, and multilayer mirrors in soft X-ray optics are some current examples. In each of these cases, the layers must resist coarsening and breakdown, which is driven thermodynamically by the free energy of the interfaces. Thus, understanding the thermodynamic forces that degrade the layering in multilayers and microlaminates is of major technological importance.

1.1. Instabilities in multilayer systems

Broadly speaking, the thermodynamic driving forces that can destroy the layering in a multilayer include chemical energy, elastic strain energy, and interfacial free energies. The drive to reduce the sum total of these energies leads to instabilities in

* Corresponding author. Tel.: +1-410-516-7069; fax: +1-410-516-5293.
E-mail address: lewisac@jhu.edu (A.C. Lewis).

the layered structure, either through mixing of the layers, atomic rearrangement, or breakdown of the layering through capillary forces.

Consider first the chemical energy between two layered elements, "A" and "B" in an "A/B" multi-layered system. When the layers contain elements that have positive heats of mixing, and therefore are immiscible, (silver/nickel or copper/niobium, for example), no intermixing that might damage the layering will occur. When the two elements have negative heats of mixing (niobium/silicon or copper/zirconium), these elements will mix and form a solid solution or compound, with the potential to destroy the layering. In addition to chemical energy, elastic strain energy can also control the stability of layered structures. Under loading, concentrations in stress and elastic strain energies can arise in the thinner sections of the layers, driving material from the thin sections to the thickest parts of the layers, where stresses are lowest [5]. Thus, diffusion should induce growth of perturbations, damaging the layering.

This paper examines the last of the thermodynamic driving forces—reduction of interfacial free energy—in detail. Current understanding [6–8] suggests that when polycrystalline layers are chemically stable and contain only small elastic strains, the ratio of grain boundary free energies and interfacial free energies (γ_{gb}/γ_{int}) controls the stability of layered polycrystalline materials. Consider a multilayered A/B material such as the Ag/Ni multilayer shown in Fig. 1(a). For polycrystalline multilayered materials such as these, there exists an equilibrium groove angle at the point where A/A interfaces (grain boundaries) meet the A/B interfaces. This groove angle is determined by the ratio of grain boundary free energy to interfacial free energy, γ_{gb}/γ_{int}, through the relationship

$$2\cos\theta = \gamma_{gb}/\gamma_{int}. \qquad (1)$$

When the ratio γ_{gb}/γ_{int} is large, significant grooving occurs where grain boundaries meet the interfaces between layers, as shown in Fig. 1(b). For sufficiently large values of γ_{gb}/γ_{int}, the grain boundary grooves can extend through layers and the microstructure is unstable. When γ_{gb}/γ_{int} is
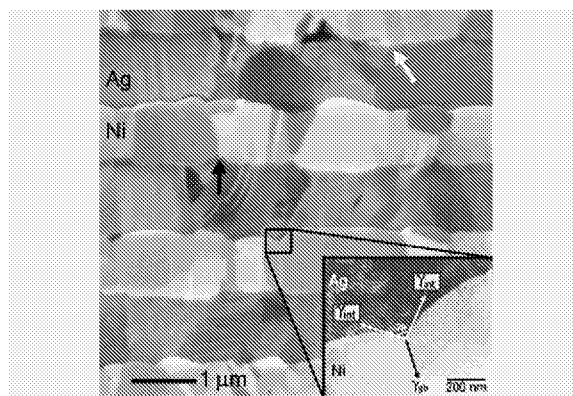

Fig. 1. Secondary electron image of a Ag/Ni multilayer annealed at 500 °C for 24 h. Note that grooves occur at the grain boundaries in both layers. (inset) Transmission electron micrograph of a Ag/Ni multilayer. The relationship between the Ni grain boundary free energy and the Ag/Ni interfacial free energy can be calculated from the angle of the groove at the junction of the three grains.

small, there is little grooving at grain boundary-interface junctions and the layering is stable.

In polycrystalline multilayer systems, the value of γ_{gb}/γ_{int} will vary both from layer to layer and from grain to grain, depending on composition and orientation. When evaluating the stability of a multilayer, the simplest approach is to neglect such variations by choosing interfacial and grain boundary free energies that are averaged for a given layer to examine general trends in layer stability. The more accurate, and considerably more difficult, approach is to consider the specific values of interfacial and grain boundary free energies that vary from grain to grain due to differences in crystallographic orientation of grains within a given layer. We examine both approaches in this paper. In the first case, we assume both layers share the same interfacial free energy, and we consider differences in average grain boundary free energies for the alternating layers. In the second case, we consider local variations within a given layer due to differences in crystallographic orientation of individual grains. *Average* grain boundary energies cited in this work represent grain boundary energies obtained using zero-creep measurements of surface energy combined with measured groove angles [9,10]. The mean value of the direct measurements is considered to be the

"average" value, with the understanding that the lowest-energy configuration is more likely to be observed, and the average surface energy and groove angles are therefore likely to be weighted with respect to this value.

2. Predicting stability in multilayers

In this first part of the study, we consider two types of stable multilayer systems: A/B systems comprised of elemental layers (i.e. Ag/Ni) and metal/compound systems comprised of alternating layers of an element and an intermetallic compound that is in chemical equilibrium with the element ("A/AB$_x$" systems, i.e. Nb/Nb$_5$Si$_3$).

First consider an immiscible elemental system, A/B. As noted in Eq. (1), the angle of the groove of one layer into an adjacent layer depends on the ratio of grain boundary free energy to interfacial free energy (γ_{gb}/γ_{int}) in each layer. Grain boundary free energies tend to scale with an element's melting temperature, as shown in Fig. 2. For this reason, the layers of the higher melting temperature material will typically have grain boundaries with higher average free energies than will the layers of the low melting temperature material. Because of the higher associated γ_{gb}/γ_{int} ratio, one would expect that, at equilibrium, deeper grooving and associated pinch-off will occur at grain boundaries in the high-T_m layers. For materials with vastly different melting temperatures, the attainment of an equilibrium groove configuration may be inhibited by the difference in diffusivity; at a given temperature, the layer with a higher melting temperature

will have the lower diffusivity. For the systems considered here at the temperatures of interest, however, diffusion is rapid enough in both layers that equilibrium is approached. In both the annealed Ag/Ni and Cu/Nb multilayer specimens shown in Fig. 3, deeper grooves are observed extending into the layer that has a higher melting temperature (Ni and Nb, respectively).

This behavior has been observed in a number of systems. Table 1 lists six A/B multilayered systems in which breakdown or coarsening has been observed. The grain boundary free energies and melting temperatures for each element are shown, and in each system, the correlation between melting temperature and grain boundary free energy is clear. The "B" layer has been defined as the element with the higher melting temperature and higher grain boundary free energy. Pinch-off or breakdown is observed in the B layers prior to the "A" layers in all cases [11–14].

Because average grain boundary free energies are not well documented for intermetallic compounds, the same comparison cannot easily be made for an A/AB$_x$ multilayer such as the Nb/Nb$_5$Si$_3$ specimen shown in Fig. 4. The *relative* value of average grain boundary free energies in A/AB$_x$ multilayers, however, can be estimated. In miscible systems that form very stable compounds, atomic mixing of elements A and B is highly exothermic ($\Delta H_{mix,A-B} \ll 0$). In such systems, the relative magnitude of interfacial free energies and grain boundary free energies can be approximated by comparing the A–A, B–B, and A–B bond energies. The energies of the A–A and B–B bonds,
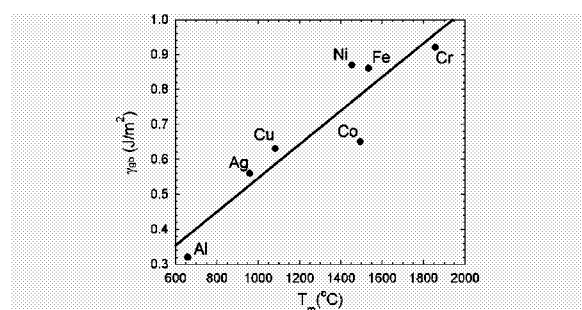
Fig. 2. Plot of melting temperature vs. average grain boundary free energy for several elements. From [10].
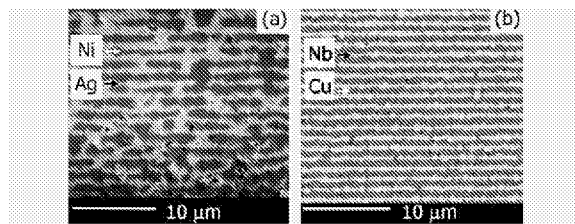
Fig. 3. SEM micrographs of two multilayer specimens. In (a), the light layers are Ag and the dark layers are Ni. The specimen was annealed at 600 °C for 72 h. Breakdown of the nickel layers is evident. In (b), the light layers are Nb and the dark layers are Cu. The specimen was annealed at 800 °C for 3 h. Pinch-off is evident in the Nb layers.

Table 1
Grain boundary free energies and melting temperatures in several elemental systems. Element B is the less stable in a laminate system

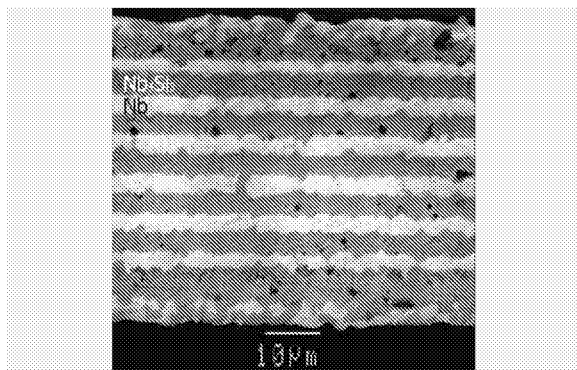| A	B	γ_{AA} (J/m^2)	T_m (A) (°C)	γ_{BB} (J/m^2)	T_m (B) (°C)	Ref.
Ag	Ni	0.56	962	0.87	1453	Current work
Ag	Fe	0.56	962	0.86	1535	[21]
Ag	Ni–Fe	0.56	962	0.87	–	[13]
Cu	Co	0.63	1084	0.65	1495	[21,22]
Cu	Nb	0.63	1084	0.76	2469	[14]
Cu	Ta	0.63	1084	0.90	3020	[12]

Fig. 4. SEM micrograph of a Nb/Nb$_5$Si$_3$ multilayered system annealed at 1500 °C for 3 h, then 1400 °C for 100 h. Pinch-off occurs in the Nb layers first.

Fig. 5. Schematic of a multilayered miscible system (A/AB$_x$). The AB$_x$–AB$_x$ grain boundaries and the A–AB$_x$ interfaces have A–A, B–B, and A–B bonds across them, and will therefore have similar energies ($\gamma_{gb}/\gamma_{int} \approx 1$ for this layer). The A–A grain boundaries have just one type of bond, A–A bonds, and will have a higher average energy than the A/AB$_x$ interface and the ratio γ_{gb}/γ_{int}, will be greater than 1. The elemental ('A') layer will therefore be less stable than the intermetallic AB$_x$ layer.

ε_{AA} and ε_{BB}, are known to be much higher than the energies of A–B bonds within the alloy, ε_{AB} (hence the heat release on formation of the intermetallic compound AB$_x$). As illustrated in Fig. 5, all three types of bonds, A–A, A–B, and B–B, are found at both the AB$_x$/AB$_x$ grain boundaries and the A–AB$_x$ interface. The elemental (A) layer, on the other hand, has primarily A–A bonds across the grain boundary. Therefore the free energies of the A/AB$_x$ interface and the AB$_x$/AB$_x$ grain boundary are likely to be similar in magnitude and much lower than the A/A grain boundary free energy, i.e.

$$\gamma_{A/ABx} \approx \gamma_{ABx/ABx} \ll \gamma_{A/A}. \tag{2}$$

Based on this relationship one can directly obtain

$$\frac{\gamma_{AB_x/AB_x}}{\gamma_{A/AB_x}} < \frac{\gamma_{A/A}}{\gamma_{A/AB_x}} \tag{3}$$

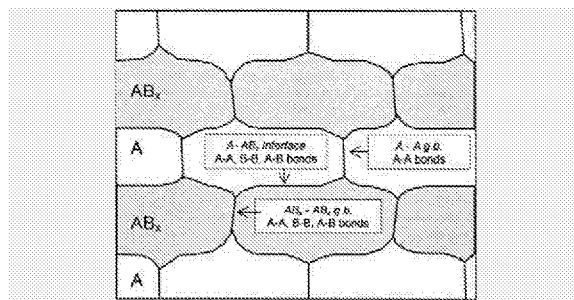which permits the prediction that the elemental layers will be subject to deeper grooving and will

be more likely to pinch off than the intermetallic AB$_x$ layers.

Consistent with the predictions, deeper grooves have in fact been observed in the elemental layers in several miscible A/AB$_x$ systems. Fig. 4 shows this phenomenon in the Nb/Nb$_5$Si$_3$ system. Table 2 lists additional A/AB$_x$ multilayer systems, and in each case, grooving is more prominent in the elemental layer, A, compared to the intermetallic compound layer, AB$_x$. As the intermetallic layers typically have the higher melting temperature (i.e., solidus), the deeper grooves in the lower melting point elemental layers might seem counterintuitive based on the earlier discussion of grooving and melting points of elemental layered materials. This clearly demonstrates why the actual energetic driving forces behind grooving must be examined as such.

The greater stability of the intermetallic layer should be beneficial in high temperature, structural

Table 2
Heat of mixing for several miscible systems. Layer A is the less stable in a laminate system

A	B	ΔH_{mix} (kJ/mol) [23]	Ref.
Nb	Nb_5Si_3	−39	[2]
Nb	Nb_3Al	−18	[24]
Mo	$MoSi_2$	−18	[25,26]
Cu	Cu_9Zr_2	−12	[27]
Nb	$NbCr_2$	−7	[28]

applications of A/AB$_x$ multilayers because the intermetallic component provides creep resistance. Pinch-off and breakdown of the elemental layer will not reduce creep resistance significantly, while breakdown of the intermetallic layer would be very detrimental to performance. The A/B elemental multilayers offer a sharp contrast. In A/B systems, the more creep resistant (high melting temperature) layer will break down first. Thus, high temperature structural applications of A/B multilayers will be limited.

3. Orientation effects

In the above discussion, average grain boundary and interfacial free energies were considered, and important trends in stability were identified. However, it is well known that the free energies of solid-solid interfaces—including grain boundaries and heterophase interfaces—depend on the crystallographic orientation of the neighboring grains [10,15]. Differences in orientation of grains within a given sample will lead to a variation in groove angles at the junction of three grains, with pinch-off being more likely in certain sets of grains than others. Thus not only can one layer be more stable than the other, but some triple junctions within a given layer will be more stable than others. Recent advances in electron backscatter diffraction and orientation image mapping [16–18] allow for high-resolution mapping of the orientation of individual grains in a polycrystalline multilayered specimen. Both in-plane and out-of-plane texture can be recorded, and can be correlated with groove angles at the junction of three grains. Because both grain boundary and interfacial free energies depend on orientation, different groove angles are expected at the junctions of grains with varying textures.

In many sputter-deposited multilayered composites, the layers will grow with a preferred texture normal to the substrate. In the Ag/Ni system, for example, both silver and nickel layers develop a $\langle 1\,1\,1 \rangle$ growth texture [19,20]. If all grains exhibit this orientation, and an epitaxial orientation relationship is preserved from layer to layer, the free energy of the Ag/Ni interface, γ_{int}, will be constant throughout the material. However, grains with other orientations do appear. Consider a multilayered system with a $\langle 1\,1\,1 \rangle$ texture, which contains some $\langle 1\,0\,0 \rangle$-type grains. Equilibrium groove angles will be calculated for four specific cases, which are illustrated in Fig. 6. The equilibrium groove angles are calculated using Eq. (1), the average grain boundary free energies for silver and nickel [10], and the calculated values of the Ag/Ni interfacial free energy that are calculated with respect to crystallographic orientation [15]. For simplicity, we will examine only cases in which the adjacent grains in the triple junction each have a $\langle 1\,1\,1 \rangle$ texture. In addition, we will use *average* grain boundary free energies. However, we will calculate equilibrium groove angles using the *specific* values for interfacial free energy, depending on whether the third grain in the triple junction has a $\langle 0\,0\,1 \rangle$ or $\langle 1\,1\,1 \rangle$ texture, as shown in Fig. 6.

In the Ag/Ni system depicted in Fig. 6(a), first consider the common junction of a $\langle 1\,1\,1 \rangle$-textured grain sitting above two adjacent $\langle 1\,1\,1 \rangle$-textured grains. For the case of a Ni $\langle 1\,1\,1 \rangle$ grain sitting above two Ag $\langle 1\,1\,1 \rangle$ grains, the Ni grain extends into the Ag layer at the Ag/Ag grain boundary with an equilibrium groove angle of 126° (Fig. 6(b)). When a Ag $\langle 1\,1\,1 \rangle$ grain sits above two adjacent Ni $\langle 1\,1\,1 \rangle$ grains, the Ag grain extends into the Ni layer with an equilibrium groove angle of 44.6° (Fig. 6(c)). Thus, as predicted previously, the Ni layer is subject to deeper grooving and is more likely to pinch off than the Ag layer.

Consider now the "off-textured" grains, where a $\langle 0\,0\,1 \rangle$ grain sits atop two $\langle 1\,1\,1 \rangle$ grains. When a Ni $\langle 0\,0\,1 \rangle$ grain meets two Ag $\langle 1\,1\,1 \rangle$ grains (Fig. 6(e)), the equilibrium groove angle is 129°, making this junction slightly more stable than the corresponding $\langle 1\,1\,1 \rangle$-textured triple junction shown in
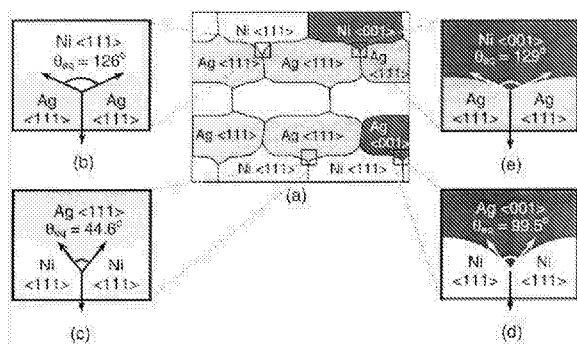
Fig. 6. Groove angles in a polycrystalline Ag/Ni multilayer. The equilibrium groove angle depends on the orientation of each grain at the triple junction.

Table 3
Equilibrium groove angles at triple junctions in the Ag/Ni system

Layer 1 (single grain)	γ_{int} (mJ/m^2)	Layer 2 (two grains and g.b.)	γ_{gb} (mJ/m^2)	θeq (°)
Ag $\langle 111 \rangle$	416	Ni $\langle 111 \rangle$	866	44.6
Ni $\langle 111 \rangle$	416	Ag $\langle 111 \rangle$	375	126
Ag $\langle 001 \rangle$	670	Ni $\langle 111 \rangle$	866	99.5
Ni $\langle 001 \rangle$	437	Ag $\langle 111 \rangle$	375	129
Ag $\langle 110 \rangle$	960	Ni $\langle 111 \rangle$	866	126
Ni $\langle 110 \rangle$	988	Ag $\langle 111 \rangle$	375	158

Fig. 6(b) ($\theta_{eq} = 126°$). When a Ag $\langle 001 \rangle$ grain meets two Ni $\langle 111 \rangle$ grains (Fig. 6(d)), the equilibrium groove angle is 99.5°, making this junction significantly more stable than the corresponding $\langle 111 \rangle$-textured triple junction shown in Fig. 6(c) ($\theta_{eq} = 44.6°$). Table 3 summarizes these comparisons, as well as others for the Ag/Ni multilayered system.

The above calculations are based on average grain boundary free energy and orientation-specific values of interfacial free energy. Because the twist and tilt angles between two adjacent grains within a layer will also affect the value of the grain boundary free energy [15], the grain boundary free energy should be calculated with respect to orientation as well. Stability can then be predicted more accurately. In systems where orientation and texture can be controlled by deposition or other fabrication methods, consideration of the free energies of the grain boundaries and the heterophase interfaces, and their dependence on orientation, should enable the design of more stable laminate systems.

4. Conclusions

In chemically stable layered systems, the free energies of the interfaces and grain boundaries frequently determine the relative stability of each layer, as well as the overall stability of the system. In immiscible metal/metal systems, the layer with the higher grain boundary free energy, which tends

to be the layer with the higher melting temperature, will be the less stable layer. In contrast, in miscible systems that form a metal/intermetallic layering, the frequently lower melting elemental layer tends to be less stable than the intermetallic layer. Understanding the texture and orientation of individual grains allows one to go even farther and predict preferential breakdown within a given layer in polycrystalline multilayers. In a Ag/Ni system with a $\langle 111 \rangle$ growth texture, triple junctions which contain $\langle 001 \rangle$-textured grains atop two adjacent $\langle 111 \rangle$ textured grains are predicted to be more stable than triple junctions containing three $\langle 111 \rangle$ grains. With an increased knowledge of grain boundary and interfacial free energies (γ_{gb} and γ_{int}), multilayer systems with enhanced stability can be designed.

References

[1] Van Heerden D, Gavens A, Foecke T, Weihs TP. Mater Sci Eng 1999;A261:212.
[2] Van Heerden D et al. Met Trans 2001;32A:2363.
[3] Gavens A, Van Heerden D, Foecke T, Weihs TP. Met Trans 1999;30A:2959.
[4] Bewlay BP, Jackson MR, Lipsitt HA. Met Trans 1996; 7A:3801.

[5] Sridhar N, Rickman JM, Srolovitz DJ. Acta Mater 1997; 45:2715.

[6] Josell D, Carter WC. In: HD Merchant, editor. Creep and stress relaxation in miniature structures and components. Minerals, Metals and Materials Society, 1996: 271.

[7] Josell D, Spaepen F. Acta Metall Mater 1993;41:3017.

[8] Josell D, Spaepen F. Acta Metall Mater 1993;41:3007.

[9] Udin H, Shaler AJ, Wulff J. Trans AIME 1949;185.

[10] Murr LE. Interfacial phenomena in materials and alloys. Reading, MA: Addison-Wellesley; 1975.

[11] Josell D, Carter WC, Bonevich JE. Nanostruct Mater 1999;12:387.

[12] Lee HJ, Kwon KW, Ryu C, Sinclair R. Acta Mater 1999;47:3965.

[13] Snoeck E et al. J Magn Magn Mater 1995;151.

[14] Troche P et al. Thin Solid Films 1999;353.

[15] Howe J. Interfaces in materials. New York: Wiley; 1997.

[16] Adams BL et al. Interface Sci 1999;7:321.

[17] Adams BL. Mater Sci Eng, A 1993;166:59.

[18] Schwartz A, Kumar M, Adams BL, editors. Electron backscatter diffraction in materials science. New York: Kluwer Academic Press; 2000.

[19] Wang Y. Trans Nonferr Met Soc China 1998;8:472.

[20] Schweitz KO et al. Philos Mag A 2000;80:1867.

[21] Josell D, Spaepen F. MRS Bull 1999;24:39.

[22] Ratzke K et al. J Magn Magn Mater 1999;204:61.

[23] de Boer FR, Pettifor DG, editors. Cohesion in metals. Amsterdam: North-Holland; 1988.

[24] Cao H, Lofvander PA, Evans AG. Mater Sci Eng, A 1994; 185:87.

[25] Kung H et al. J Vac Sci Technol, B 1995;13:1126.

[26] Torri P et al. J Vac Sci Technol, A 1999;17:1329.

[27] Weihs TP, Barbee TW. Acta Mater 1997;45:2307.

[28] Rowe RG, Skelly DW, Larsen M. Scr Metall Mater 1994; 31:1487.