

Interface stresses and their effects on the elastic moduli of metallic multilayers

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The embedded-atom method is used to calculate the surface stresses and the interface stresses for several fcc metals and interfaces between them. While the surface stresses are all positive (i.e., they tend to put the underlying crystal in compression), in several instances (e.g., in the Pt/Ni system) negative interface stresses are found. The effects of the interface stresses on the elastic moduli of metallic multilayers are discussed.

INTRODUCTION

The properties of metallic heterophase boundaries have attracted considerable attention in recent years because of the important role these interfaces play in determining the physical properties of materials. The enhanced biaxial modulus which has been found in compositionally modulated metallic multilayers¹ is one where the interface properties become macroscopically important. For systems involving layered fcc metals [e.g., Cu/Ni (Ref. 2) or Au/Ni (Ref. 1)] twofold and higher enhancements in the in-plane biaxial modulus $Y[111]$ have been reported for composition modulations of approximately 2 nm wavelength. This so-called *supermodulus effect* is, however, absent in other systems like the Cu/Au system.³

There are at present three approaches towards understanding the supermodulus effect. The first approach is based on changes in the electronic structure owing to interaction of the Fermi surface with the reduced Brillouin zones created by the multilayer superlattice.⁴ A peak in the modulus as a function of compositional wavelength appears where this Fermi-surface-Brillouin-zone interaction (FSBZI) is most effective. At present, however, the FSBZI models do not seem sufficiently developed to allow for a quantitative analysis of the supermodulus effect⁵ and seem to show some contradictions to other experimental observations.⁵ The second approach seeks to explain the supermodulus effect by nonlinear elastic effects generated by large biaxial strains in a coherent superlattice.⁶ In this *coherency strain model* a decrease of the moduli for longer-wavelength composition modulation is attributed to the loss of coherency and the introduction of misfit dislocations. An embedded-atom method (EAM) model of coherent Cu/Ni superlattices, which should be able to represent all relevant parameters of the coherency strain model, however, showed no supermodulus effect,⁷ but only a slightly increased biaxial modulus. The third and most recent approach seeks to explain the supermodulus effect as due to nonlinear elastic effects caused by elastic, biaxial strains generated by interface stresses in semicoherent interfaces.⁸ As the distance between the interfaces decreases, the biaxial

modulus of the multilayer package increases. A subsequent decrease of the biaxial modulus at very small distances is then attributed to the possible formation of coherent interfaces. Although this *interface-stress model* is plausible, it still has to be proven that the interface stresses have the correct order of magnitude to account for the large reported modulus enhancements and that they have the correct sign, i.e., that they are tensile.

The concepts of interface energy and interface stress can be introduced in analogy to the surface energy and surface stress concepts (e.g., Ref. 9, and references therein). Although these concepts of energies and stresses have to be carefully distinguished in solids, one still often finds that no distinction is drawn between them and that interface stress or interface tension is used where interface energy is meant. In spite of both concepts having their own range of applicability, to our knowledge there has been no attempt so far to calculate interface stresses at heterophase boundaries. All atomistic calculations have been focused on the interface energy only.

We attempt here to calculate the surface and interface stresses for several fcc metals and interfaces between them. We will therefore first explain the concept of interface stress in relation to interface energy and describe how to calculate interface stresses for multibody potentials like the EAM.¹⁰ We will then present our results for the interface stresses in epitaxial, parallel oriented (100) and (111) interfaces in the Ag/Ni, Ag/Cu, Pt/Ni, Au/Ni, and Au/Cu systems. We find the interface stresses are too low to fully account for the strongly enhanced moduli found experimentally. In the case of Pt/Ni the interface stress is even negative.

INTERFACE ENERGY, INTERFACE STRESS

The interface energy γ of a heterophase boundary is the energy required to form new interface area by increasing the number of atoms at the interface. Alternatively, the interface energy γ can be interpreted as the sum of the excess energies of all atoms in a region around the interface. The excess energy is then defined as the difference between the actual energy of an atom and the

energy it would have in an ideal homophase crystal in the same deformation state. Although the treatment here should properly be made in terms of the Gibbs free energy if we intend to compare to experiments, we are in the following dealing with internal energies only, because our calculations are restricted to internal energies at zero temperature.

The interface energy can be measured in an idealized cleavage experiment, where an interface is fractured to create two different surfaces. If no dissipative processes are involved in this cleavage experiment, the work of adhesion W_{ad} is

$$W_{\text{ad}} = \gamma_A + \gamma_B - \gamma_{A/B}. \quad (1)$$

γ_A , γ_B , and $\gamma_{A/B}$ represent the surface energy of materials A and B and the interface energy. Another experiment to obtain relative interface energies is the measurement of dihedral angles at triple junctions of different crystals. Because the interface energies are highly anisotropic with respect to the parameters defining the orientation of the interface, care must be taken to account for torque terms.¹¹

The interface-stress tensor $\tau_{\alpha\beta}$ is defined as the in-plane strain derivative of the total interface energy ($A\gamma$) per unit area A :

$$\tau_{\alpha\beta} = A^{-1} \frac{\partial(A\gamma)}{\partial \epsilon_{\alpha\beta}}. \quad (2)$$

The interface-stress tensor is isotropic on (100) and (111) boundary planes. The (average) interface stress may then also be expressed as

$$\tau = \gamma + A \frac{\partial \gamma}{\partial A}. \quad (3)$$

The interface stress can therefore be interpreted as the energy required to increase the interface area but keeping the number of atoms at the interface constant. A positive interface stress tends to decrease the interface area.

We model the atomic interaction using the EAM.^{10,12} The total energy of an ensemble of atoms is given as the sum of a pairwise interaction V and a function $F(\rho)$ in which ρ is the local density:

$$E = \sum_i F_{v_i}[\rho_i] + \frac{1}{2} \sum_i \sum_{j(\neq i)} V_{ij}, \quad (4)$$

where

$$\rho_i = \sum_{j(\neq i)} \rho_{v_j}^a(R_{ij}), \quad V_{ij} = \frac{Z_{v_i}(R_{ij})Z_{v_j}(R_{ij})}{R_{ij}},$$

where v_i , v_j indicate whether the functional form for the species of atom i or atom j is used. R_{ij} is the distance between atom i and atom j . [The different functions in Eq. (4) are explained in detail in Ref. 12. We use the same notation.] The derivation of the surface stress tensor for this type of multibody interaction has been given by Ackland and Finnis.⁹ We do not repeat this derivation here for the interface-stress tensor but give the final expression:¹³

$$\tau_{\alpha\beta} = \frac{1}{A} \sum_i \sum_{j(\neq i)} \left(\frac{\partial F_{v_i}}{\partial \rho_i} \frac{\partial \rho_{v_j}^a}{\partial R_{ij}} + \frac{1}{2} \frac{\partial V_{ij}}{\partial R_{ij}} \right) \frac{R_{ij\alpha} R_{ij\beta}}{R_{ij}}. \quad (5)$$

CALCULATIONS AND DISCUSSION

We calculate the interface stresses of epitaxial, parallel oriented interfaces on the (100) and (111) boundary planes in the following systems: Ag/Ni, Ag/Cu, Pt/Ni, Au/Ni, and Au/Cu. All systems have a large misfit of 10% or more and therefore are expected not to form coherent interfaces even for very thin layers. The interfaces are formed by putting two ideal crystals together, which results in a chemically abrupt interface. A supercell geometry is used with periodic boundary conditions applied in the plane of the interface. The naturally incommensurable interfaces are thereby forced into an n/m coincidence and the residual misfit is accommodated elastically. The n/m ratios which have been used are given in Table II. We model the bicrystals with free surfaces parallel to the interface. The distance between the surfaces and the interface has been chosen to always exceed 4 nm. Several test calculations have been carried out to ensure that this model thickness is large enough to prevent interaction between the surfaces and the interface. The interfaces are then relaxed using a variable metric conjugate gradient method. The relaxation always leads to the formation of misfit dislocation networks. Compositional changes at the interface do not occur during this energy minimization procedure. The surface energies and stresses and the interface energy and stress are then calculated in the same relaxed configuration. Because of the residual misfit in the supercell, Eq. (5) cannot be used directly for the calculation of the surface and interface stresses. We have to subtract the residual stresses for each crystal, which are measured in the bulklike region halfway between the surface and the interface. It is shown below that this method of calculating surface and interface stresses is convergent if the residual misfit is small enough.

The results for the surface energies and stresses are given in Table I. Energies and stresses are both of the same order of magnitude, indicating that the second term in Eq. (3) is of the same order of magnitude as the surface energy. All surface stresses are positive, i.e., tend to compress the underlying crystal, which has been suggested to be a criterion for the stability of the lattice which is modeled.⁹ The surface stress tends to be lower than the surface energy for the lighter elements Cu and Ni [especially on the (111) surfaces]. In contrast, the heavier $5d$ elements Pt and Au show higher surface stresses by up to a factor of 2 as compared to the surface energies. These relatively high surface stresses for Au could be interpreted¹⁵ to be the driving force for the $23 \times \sqrt{3}$ reconstruction on the Au(111) surface, which appears to involve the insertion of an extra row of atoms into the surface every 23 rows.¹⁴

The accuracy to which we determine the surface stresses will be discussed in the following. First we recall that all surface stresses are calculated in slightly strained lattices because of the residual misfit in the bicrystals. This residual misfit leads to biaxial strains up to 0.5%. The difference between the surface stresses in the unstrained and in the strained configuration has been calculated for Ni as an example and turns out to be less than

TABLE I. Surface energies γ and stresses τ of the (100) and (111) surfaces calculated for several fcc metals using the EAM. For comparison, data from pseudopotential calculations (Ref. 15) are given in parentheses. (All entries are in units of J/m^2 .)

Surface orientation	Ni	Cu	Ag	Pt	Au
(100) γ_{100}	1.57	1.29	0.70	1.64	0.92
τ_{100}	1.27	1.38	0.82	2.69	1.79
(111) γ_{111}	1.44	1.18	0.62	1.44(2.20)	0.79(1.25)
τ_{111}	0.43	0.86	0.64	2.86(5.61)	1.51(2.77)

$2 \times 10^{-2} \text{ J/m}^2$. The numerical errors are of the same order of magnitude. The largest uncertainty, however, is in the choice of the interatomic interaction. Calculations of surface stresses using different EAM potentials which were all fitted to the same material properties revealed significant differences in the surface stresses while giving much smaller differences in the surface energies.¹⁶ Similarly, comparing our results with the surface energies and stresses calculated with Finnis-Sinclair potentials¹⁷ for Ni, Cu, Ag, and Au (Ref. 18) we find that the surface energies γ agree within $\pm 20\%$, but that the surface stresses τ differ by up to $\pm 50\%$. However, the general tendencies, τ being larger than γ for Au and τ_{111} being smaller than γ_{111} for Ni and Cu, are the same. More fundamental methods have only been applied to the calculation of surface stresses on the Pt and Au(111) surfaces.¹⁵ The results of these pseudopotential total energy calculations are given in parentheses in Table I. Both surface energies and stresses are higher than our values, but show again that τ is significantly larger than γ for Pt and Au.

The relatively large scatter in the surface stresses resulting from different interaction parameters suggests that we should emphasize qualitative conclusions rather than precise numerical results. For the calculation of the interface stresses we expect the quantitative data to be more reliable.

The calculated interface stresses and interface energies are summarized in Table II. The approximate ratio of the lattice constants used for the determination of the periodic lengths and the mutual heats of solution (from Ref. 12) are also given in Table II. The interface stresses and energies are of the same order of magnitude and are even more closely correlated than the surface stresses and

energies. A common characteristic of all systems is that the interface energies on the (111) boundary planes are lower than on the (100) boundary planes. This can be attributed to the smaller structural contribution (which will be explained in what follows) to the interface energy on (111) planes than on other boundary planes.¹⁹ In consequences τ_{111} is also always lower than τ_{100} .

The appearance of negative interface stresses and negative interface energies in Table II seems surprising at first sight. However, the negative interface energy γ_{111} for the Pt/Ni system can be understood if we introduce the idea that the interface energy of a semicoherent heterophase boundary²⁰ contains a chemical component, which arises from the chemical inhomogeneity in the interface region, and a structural component due to the distortions associated with misfit dislocations. (See Ref. 19 for details.) The chemical component should be negative for all chemically abrupt interfaces in miscible systems with negative mutual heats of solution.²¹ If it is also larger in absolute value than the structural component, a negative semicoherent interface energy is obtained. Negative interface stresses may also appear on boundaries with positive interface energy, because the sign of the second term in Eq. (3) can be either positive or negative. Following these arguments we expect a loose correlation of the interface stresses and energies with the mutual heats of solution, which is present in our results on the (100) boundary plane as well as on the (111) boundary plane, as seen in Table II.

The effect of interface stresses on the biaxial modulus of metallic multilayers should be such as to increase the biaxial modulus with increasing (positive) interface stress and decreasing distance between the interface.⁸ The in-

TABLE II. Compilation of the interface stresses τ and energies γ calculated for several parallel oriented metal-metal bicrystals using the EAM. The mutual heats of solution for single substitutional impurities represented by these EAM potentials (from Ref. 12) and the relative lattice periodicities are given as well. Their relation to the interface stresses and energies is explained in the text.

Bicrystal A/B	Ratio of the lattice constants a_A/a_B	Alloy heats of solution		(100) interface		(111) interface	
		A in B (eV)	B in A (eV)	γ_{100} (J m^{-2})	τ_{100} (J m^{-2})	γ_{111} (J m^{-2})	τ_{111} (J m^{-2})
Ag/Ni	6/7	0.42	0.38	0.82	0.83	0.42	0.32
Au/Ni	6/7	0.30	0.08	0.54	0.71	0.14	-0.08
Ag/Cu	7/8	0.11	0.18	0.47	0.53	0.24	0.32
Au/Cu	7/8	-0.18	-0.12	0.29	0.33	0	0.01
Pt/Ni	9/10	-0.28	-0.25	0.32	0.04	-0.12	-0.57

interface stresses which are necessary to give a modulus enhancement of 50% at the experimentally measured composition modulation wavelength have been estimated to be of the order of J/m^2 .⁸ Our calculated interface stresses are all below 1 J/m^2 and are especially low for the (111) boundary plane on which most of the experiments are performed. Even if we do not address specific systems, we may therefore conclude that the interface stresses seem to be too low to fully account for the observed modulus enhancements. The negative interface stresses we observed should even give a decrease in the in-plane biaxial modulus of a multilayer package.

Addressing specific systems, we may first look at the Au/Ni and Au/Cu systems. A strong Y [111] biaxial modulus enhancement was found experimentally for Au/Ni multilayers,¹ while no such Y [111] modulus enhancement was found in Au/Cu multilayers.³ We find vanishing interface stresses for both Au/Ni and Au/Cu(111) interfaces. While the lack of a modulus enhancement in Au/Cu multilayers is consistent with a vanishing interface stress, the modulus enhancement in Au/Ni multilayers cannot be explained using the interface-stress model. Following our above argument based on the dependence of τ on the mutual heats of solution, we expect the Ag/Pd and Cu/Pd systems to have small or even negative interface stresses because of their negative mutual heats of solution. Both systems, however, show the enhancement in the Y [111] biaxial modulus in multilayer superlattices.^{1,3}

A drawback of our analysis of the interface-stress model certainly is the unknown accuracy in the determination of τ connected with the use of the EAM potentials, although the EAM probably represents the best available description of the interatomic interaction for these purposes. Another problem of our model is the use of chemically abrupt interfaces for the determination of the interface stresses. It is yet unknown how an intermixing at the interface affects the effective interface stress.

Although we have shown that the interface stresses are too low to fully account for the observed modulus enhancements, they have to be taken into account in a careful model of the supermodulus effect. On the other hand, surface and interface stresses may play an impor-

tant role in epitaxy as well. As pointed out by Cammarata and Sieradzki,⁸ surface and interface stresses should cause a thin epitaxial overlayer to relax into a strained condition and this should be considered in the energy balance of equilibrium elastic theories determining the maintenance of coherency. Also, an unexpected behavior may be obtained in some specific systems. Let us, for example, consider a thin film of Ni deposited on a Pt(111) substrate. Our results would suggest that the high surface tension of the Pt surface should be transferred to a negative effective stress after the deposition of the Ni film. Similarly, the deposition of Ni on a Au(111) surface should relieve the strong surface tension, which is assumed to be the driving force for the $23 \times \sqrt{3}$ surface reconstruction on this surface. One would then expect either a buckling of the Au surface or a heavily compressed layer of Au at the interface. While these predictions seem rather speculative at the present state, we hope that our results may stimulate some further work on this subject.

In summary, we have presented a calculation of the interface stresses in epitaxial, parallel oriented (100) and (111) metal-metal boundaries. The negative interface stress in the Pt/Ni system could be explained by the strongly negative chemical contribution to the interface stress, which has its origin in the formation of a chemically abrupt interface in an otherwise miscible system. As a general tendency, we found that the interface stresses are too low to fully account for the strongly enhanced moduli of metallic multilayers observed experimentally. They should, however, be considered in the modeling of the supermodulus effect as well as in theoretical treatments of epitaxy.

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- ²⁰In coherent interfaces the chemical component is the only contribution to the interface energy.
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