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Tuning phase stability in nanocomposite multilayers

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As thin-film layers in a multilayered stack are reduced in thickness, changes in phase stability can result within the individual layers. These changes in phase are expected to have a significant influence upon the functional properties of the nanostructured composite. The ability to engineer, or tune, phase stability at this nanometer length scale is of significant importance in order to maximize the functional properties of these materials. We report the prediction and experimental conformation of tuning the *hcp* to *bcc* phase stability in Ti for Ti/Nb multilayered nanocomposites. The prediction was based upon selective alloying of Ti with a *bcc* β stabilizing element using a new form of a thermodynamic phase diagram for predicting phase stability in thin-film multilayers. © 2003 American Institute of Physics. [DOI: 10.1063/1.1620671]

In a recent report,¹ it was postulated that alloying could be used as an engineering mechanism for tuning metal carbide thin-film multilayers to restrict dislocation motion. As the phase stability of the individual layers within the metal carbide stack is altered, the change in the chemical and structural components at the interface could either hinder or facilitate dislocation propagation between layers. In this letter, we provide a predictive methodology with subsequent experimental confirmation that alloying can be used to tune phase stability in nanocomposite thin-film multilayers. The application of this methodology can be used not only to enhance the mechanical strength of multilayers, but also to influence other potential functional properties in magnetic recording and semiconductor devices.

It is well established that in the early stages of thin film growth, a thin film can adopt a phase that is not the expected equilibrium structure of that material. This has been referred to as pseudomorphic growth.^{2,3} Examples include *hcp* Ir on Ru,⁴ *bcc* Pd on W,⁵ and *fcc* Fe on Pt.⁶ Similar pseudomorphic phases have been reported in multilayered thin films, such as *bcc* Cr in Cr/Co,⁷ *hcp* Co in Cr/Co,⁸ *fcc* Ti in Ti/Al,⁹ and *bcc* Zr in Zr/Nb.^{10,11} The present authors have recently reported a change in phase stability from *hcp* Ti to *bcc* Ti in sputtered deposited Ti/Nb multilayers.¹² The *hcp* to *bcc* phase stability can be understood as the competition between the volumetric and interfacial free energy components of the total free energy of the Ti/Nb system.¹³ As the Ti layers were reduced in thickness, for a fixed bilayer spacing λ , which is equivalent to the Ti layer thickness plus the Nb layer thickness in a repeating compositional modulation, the Ti layer adopted a *bcc* structure. By varying the volume fraction of Nb, or equivalently the individual Nb layer thickness within the Ti/Nb unit bilayer for fixed bilayer spacings, the critical layer thickness for *hcp* to *bcc* phase stability in Ti was altered. The total free energy of the Ti/Nb multilayer can be represented by this unit compositionally modulated bilayer of Ti/Nb as¹³

$$\Delta G/A = \Delta g = \Delta G_{\text{Ti}}(1 - f_{\text{Nb}})\lambda + 2\Delta\gamma, \quad (1)$$

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where $\Delta G/A$ is the total free energy change between the pseudomorphic and equilibrium phases normalized by the fixed surface area of the film, ΔG_{Ti} is the volumetric free energy difference between *bcc* and *hcp* Ti, f_{Nb} is the volume fraction of Nb within the repeated bilayer, λ is the bilayer spacing defined earlier, and $\Delta\gamma$ is the interfacial free energy difference between the *bcc*-Ti/*bcc*-Nb and *hcp*-Ti/*bcc*-Nb interface. A change in phase stability from the equilibrium phase will result in an increase in the volumetric free energy term, ΔG_{Ti} ; therefore, the stabilization of a pseudomorphic phase requires a specific combination of length scale λ , and volume fraction f_{Nb} , such that the interfacial free energy component $\Delta\gamma$, a negative value, is sufficient to lower the total free energy Δg . To maintain the simplicity of Eq. (1), all terms that scale with volume, such as strain, and all terms that scale with area will be included in the respective ΔG or $\Delta\gamma$ terms. The additional complexities of such factors can be individually separated out of the generic ΔG or $\Delta\gamma$ terms and be discretely treated within the context of Eq. (1) as needed.^{11,13} A detailed derivation of Eq. (1) can be found elsewhere.¹³

In this model, the total free energy for the stabilization of a pseudomorphic phase has two degrees of freedom, either the bilayer thickness λ , or the volume fraction f_{Nb} . A plot of the inverse of the bilayer spacing versus the volume fraction of Nb provides a clear representation of the interdependent relationship between the phase stability and these two degrees of freedom. This type of plot has been referred to as a biphasic stability diagram¹³ in that it represents the phase stability of two phases, Ti and Nb. The experimentally determined biphasic diagram for Ti/Nb is shown in Fig. 1(a).¹² The change in phase stability from *hcp* Ti to *bcc* Ti is clearly evident in Figs. 1(b) and 1(c) by the loss in the two textured peaks of *hcp* Ti {0002} and *bcc* Nb {011} to a single *bcc* Ti and Nb {011} peak. The high temperature lattice parameter of *bcc* β -Ti extrapolated to room temperature is 3.28 Å, which is nearly equivalent to 3.30 Å lattice parameter of *bcc* Nb. This allows for a coherent interface to form with negligible coherency strains.¹² From Eq. (1), the slope of the Fig. 1 boundary can be derived to be

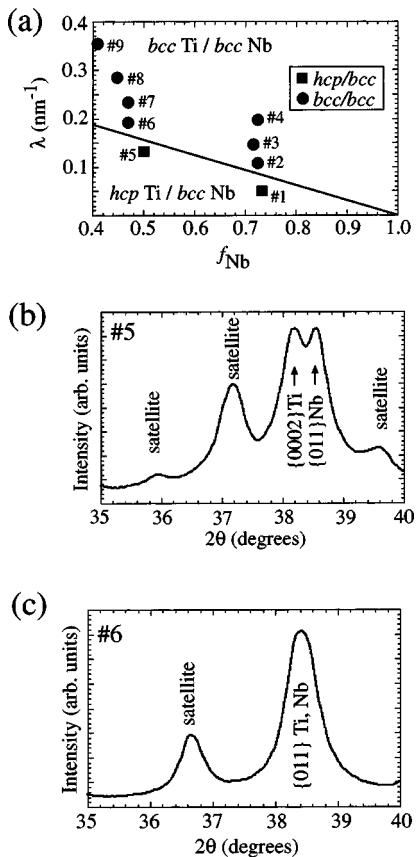


FIG. 1. (a) The *hcp* to *bcc* biphase stability diagram for Ti/Nb multilayers (see Ref. 12). (b) XRD pattern for Ti/Nb #5. The textured growth of the closest packed planes of the *hcp* Ti and *bcc* Nb phases are present. (c) XRD pattern for Ti/Nb #6. The Ti layer has undergone a change in phase stability from *hcp* to *bcc* with a reduction in the bilayer spacing as evident by the diffraction of a single {011} peak.

$$\text{slope} = \Delta G_{Ti}/2\Delta\gamma. \quad (2)$$

Since the phase stability boundary's slope is equivalent to the ratio of the free energies, the alloying of the Ti layer with either an α (*hcp*) stabilizer or a β (*bcc*) stabilizer should alter the slope of the phase stability boundary and consequently the critical transition layer thickness for stabilizing the pseudomorphic phase. Table I is a listing of the free energies for this system used in the calculations. It should be noted that while alloying the Ti layer alters the value of ΔG_{Ti} , it might also influence the value of $\Delta\gamma$. Possible influences of the alloying on the value of $\Delta\gamma$ include a change in the misfit between the Ti and Nb layers or a change in the crystallographic orientation relationship between these layers. Such changes in the value of $\Delta\gamma$ will directly influence the slope of the phase stability boundary and consequently the critical transition layer thickness associated with the *hcp*-*bcc* transformation in the Ti layers. Thus, if the value

TABLE I. Free energies used in the calculation to predict the phase stability of Ti layers in Ti/Nb multilayers with the addition of V. Note that the interfacial free energy was calculated from the slope, Eq. (2), of the phase boundary on the biphasic diagram.

| Multilayer | $\Delta\gamma$ (mJ/m ²) | $\Delta G_{bcc-hcp}$ (J/m ³) | Ref. |
|------------|-------------------------------------|--|------|
| Ti/Nb | ≈ -583 | $(\Delta G_{Ti}) 3.5 \times 10^8$ | 15 |
| Ti-8V/Nb | ≈ -570 | $(\Delta G_{Ti-8V}) 2.5 \times 10^8$ | 14 |

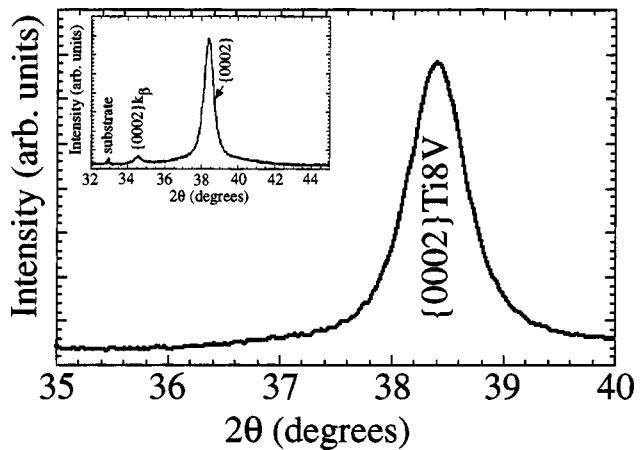


FIG. 2. XRD scan profile of a 600-nm-thick Ti-8V thin film. The presence of a single {0002} peak indicates that the film has deposited as a single phase of super saturated solid solution of *hcp* α -Ti. The inset pattern is a wider scan of the film.

of $\Delta\gamma$ decreases substantially, it could in principle negate the effect of reduction in ΔG_{Ti} as a result of the alloying, and consequently not lead to an increase in the thickness to which the pseudomorphic *bcc* Ti phase can be stabilized. Another important point to be noted is that the content of the alloying element in the Ti layers should be restricted to the limit of maintaining a single phase solid solution in the as-deposited thin film. If the alloying leads to the formation of multiple phases in the as-deposited Ti layers, Eq. (1) is no longer applicable, and therefore the phase stability in the layers cannot be predicted using the simple model used in this letter.

To test this proposed concept, a Ti 8 at. % V (Ti-8V) sputtering target was prepared by vacuum arc melting. Vanadium, a *bcc* β stabilizer, should help to facilitate the *hcp*-to-*bcc* phase stability of Ti in the Ti/Nb multilayers. The multilayers were sputtered deposited in an UHV stainless steel chamber that has a base pressure of $\approx 4 \times 10^{-9}$ Torr. Ultrahigh-purity Ar was used as the working gas at a pressure of 2–3 mTorr. Room temperature Si [001] wafers, with native oxide on the surface, were automatically rotated between the Ti-8V and Nb sputtering targets for the deposition of a set of 40 bilayer multilayers with varying bilayer spacings and volume fractions. The multilayers were characterized in the as-deposited state (on the substrate) in the Bragg-Brentano geometry using a Scintag XDS 2000 Diffractometer operating with Cu K α radiation at 45 kV and 20 mA with a scan rate of 0.5°/min at a chopper increment of 0.03°. As seen in Figs. 1(b) and 1(c), the films grew with a preferred out-of-plane texture that corresponded to their closest packed planes; for example {011} *bcc* and/or {0002} *hcp*.

The solid solubility of V in Ti at room temperature is approximately 2 at. %. The Ti-8V thermodynamic equilibrium composition places it in the $\alpha + \beta$ phase field. The microstructural presence of β -Ti in the α -Ti layers would require the additional volumetric and interfacial free energy contribution with the corresponding volume fraction to be added to Eq. (1). But sputtering is inherently a nonequilibrium process with rapid quench rates that can allow for a single-phase supersaturated solid solution to be deposited.

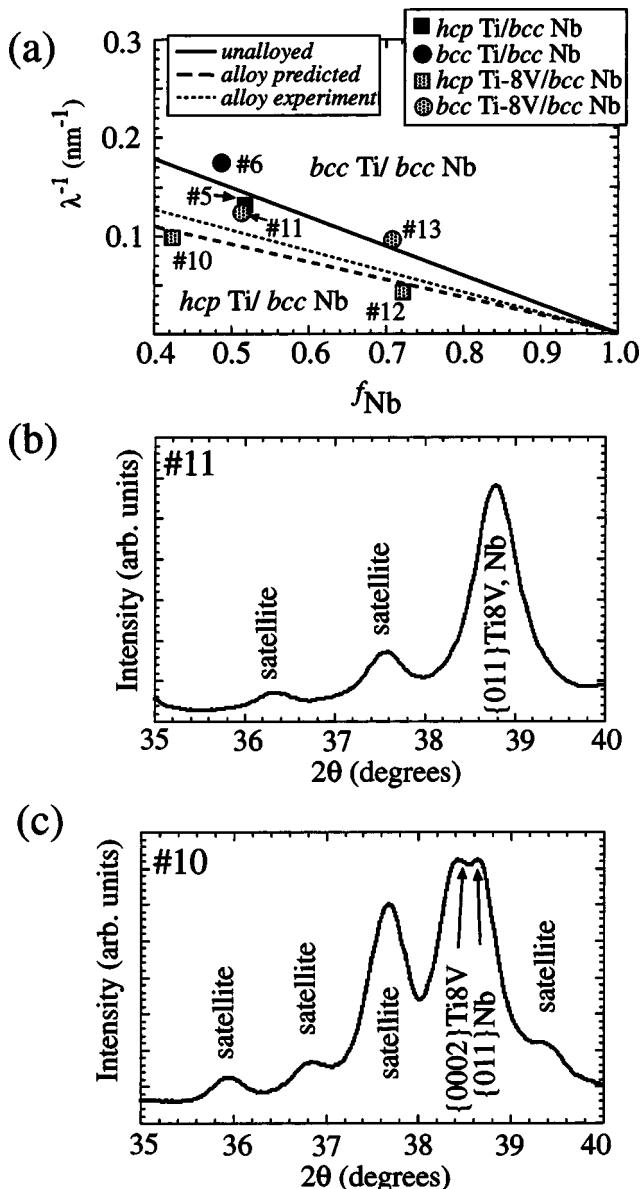


FIG. 3. (a) Biphase stability diagram of Ti-8V/Nb multilayers. The solid line represents the phase boundary for the unalloyed Ti/Nb multilayers whereas as the dashed line represents the predicted boundary for the alloyed Ti-8V/Nb multilayers. The data points indicate the facilitation of *bcc* phase stability in the Ti layers with good agreement with the predicted boundary, indicated by the dotted line. (b) XRD pattern for the Ti-8V/Nb #11 specimen. For a nearly equivalent position on the biphasic diagram as Ti/Nb #5, the alloyed multilayer has facilitated the *bcc* phase stability, as evident by the single $\{011\}$ peak [cf., Fig. 1(b)]. (c) XRD pattern for the Ti-8V/Nb #10 multilayer. With an increase in the bilayer spacing, the alloyed Ti-8V layers revert to the *hcp* phase, indicated by the two textured peaks, *hcp* $\{0002\}$ and *bcc* $\{011\}$ [cf., Fig. 1(c)].

This was successfully achieved for a 600-nm α -Ti-8V film grown at room temperature on Si [001]. The x-ray diffraction (XRD) scan in Fig. 2 of this film diffracts a single textured *hcp* α -Ti $\{0002\}$ peak. The presence of β -Ti would result in a splitting of this peak into the $\{0002\}$ and $\{011\}$ intensities. The presence of a single α -Ti phase allows the model given in the form of Eq. (1) to be applicable.

Assuming a similar interfacial free energy reduction $\Delta\gamma$ as Ti/Nb,¹² listed in Table I, a first approximation of the boundary, using Eq. (2), has been plotted as a dashed line onto Fig. 3(a) for a corresponding change in the volumetric

free energy for Ti-8V/Nb multilayers. It should be noted that ΔG_{Ti-V} actually represents the difference in magnitude of G_{Ti-V} (*bcc*) and G'_{Ti-V} (*hcp*), where G'_{Ti-V} is the free energy of the supersaturated *hcp* Ti-V solid solution of composition Ti-8V¹⁴ listed in Table I. Note that the G'_{Ti-V} (*hcp*) $> G_{Ti}$ (*hcp*). Based upon this predicted boundary for the facilitation of *hcp* to *bcc* phase stability, a series of Ti-8V/Nb multilayers were sputtered deposited.

It is evident from the data points in Fig. 3(a) that the addition of the β stabilizer has facilitated the *bcc* phase stability within the Ti layers. The XRD pattern on Fig. 1(b) is for an unalloyed *hcp*-Ti/*bcc*-Nb multilayer with $\lambda = 7.5$ nm and $f_{Nb} = 0.51$. The bilayer spacing was confirmed from the separation of the satellite reflections that arise due to the chemical modulation of the multilayer stack in the XRD pattern where the volume fraction was calculated from an energy dispersive spectrum using a Philips XL 30 scanning electron microscope. From this figure the split in the *hcp* Ti $\{0002\}$ and *bcc* Nb $\{011\}$ peak is present. For a nearly equivalent Ti-8V/Nb multilayer (#11) with $\lambda = 7.4$ nm and $f_{Nb} = 0.50$, a single $\{011\}$ peak is present in Fig. 3(b). This change in phase stability to a *bcc/bcc* multilayer as compared to the unalloyed multilayer confirms the facilitation of *bcc* phase stability. The *hcp*-Ti-8V/*bcc*-Nb XRD scan for point #10 is shown in Fig. 3(c) and exhibits good agreement with the prediction. This suggests that controlled alloy content within the Ti layer could allow tuning the phase boundary to a specific volume fraction and length scale for a particular multilayer.

In this letter a thermodynamic methodology was used in the prediction and subsequent confirmation of tuning the *hcp* to *bcc* phase stability in Ti for Ti/Nb multilayers. The alloyed deposited multilayers exhibited good agreement with the predicted change in the slope of the phase stability boundary between these two phases. The ability to engineer these nanocomposite films could have applicability in the enhancement of a particular property as a function of phase.

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