Combinatorial studies of mechanical properties of Ti–Al thin films using nanoindentation

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Abstract

In this paper, we describe an on-going effort to develop a thin film combinatorial method for identifying alloy compositions of potential interest as structural materials. To investigate this idea, compositionally graded Ti–Al thin films have been sputter deposited onto Si substrates, and the mechanical properties of the “library” of compositions are then probed using nanoindentation. This combinatorial method offers the possibility of rapidly varying the compositions and microstructures of alloys and quickly determining the compositions and microstructures of greatest interest for further development as bulk structural alloys. Nanoindentation experiments are used to extract the properties of the film so that the bulk properties of the material may be estimated. A new method for extracting the hardness of films on substrates from nanoindentation experiments has been developed and is applied to the compositionally graded Ti–Al thin films. Together with the nanoindentation data and a compositional analysis, we are able to establish a relationship between the hardness of the film and the composition. We discuss the results of these combinatorial experiments in connection with estimating the properties of bulk materials.

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1. Introduction

Combinatorial materials science involves high-efficiency methods for creating “libraries” of material compositions that can be quickly scanned for different properties of interest. These techniques are especially beneficial in searches for material properties that might depend on many different compositional and microstructural factors. In such cases, the high-throughput combinatorial technique can facilitate the discovery of material compositions, microstructures, etc., that might profit from more intense investigations, while minimizing the required time, effort, and cost compared with the “one-at-a-time” synthesis and analysis methods.

Current sample synthesis technology allows for the creation of a “library” of compositions using several different methods. The precursor method, used in creating phosphor thin-film libraries [1], involves sample synthesis from multiple-layered precursor depositions using a movable mask, followed by a thermal annealing step to allow inter-diffusion of the layers to form the final phases. This method relies on favorable thermodynamics and kinetics to form the desired reaction product during the annealing step, and thus is not a universal technique for preparing samples. Other methods of synthesis involve creating a spread of compositions using various high-vacuum thin-film deposition approaches including sputtering, laser ablation, ion-beam
deposition, thermal and electron beam evaporation. To create the needed composition variations, different mask strategies have been reported to be successful: shadow masks [2,3], lithographic masks [1], and movable shutter masks [4,5]. The use of a natural thickness gradient in thin films deposited using the multi-target deposition geometry is a simpler technique that can be used to successfully create large composition gradients in a single sample [6]. Although multi-target deposition has been used to grow films with varying compositions [7–9], the typical approach has been to use two or three targets, each with different elements. This approach gives a non-linear composition profile and a large variation in film thickness for cases where there is a large difference in the deposition rate from each gun. Our four-target approach, described below, results in a much more nearly linear composition profile and a film thickness that is nearly uniform despite a large difference in flux.

Combinatorial chemistry has been successful in developing promising pharmaceuticals, phosphors, and catalysts, but this method has only recently been extended to bulk structural materials through the creation of libraries of compositions formed in diffusion couples and tested subsequently by nanoindentation [10]. Structural alloys with desired mechanical properties usually contain several alloying elements, and the properties can depend on many other factors such as microstructure, grain size, etc. Thus, the combinatorial method may be useful for the empirical process of identifying the optimal combination of materials for further development.

Combinatorial studies of thin film samples using the natural gradients that exist in the multi-target sputter deposition process have some advantages over the bulk diffusion couple sample approach. The diffusion couple samples require several tedious and time consuming processing steps to achieve the final form for mechanical property evaluation. Thus, the use of thin film “libraries” created by sputter deposition might provide a more time and cost effective way to implement combinatorial studies of mechanical properties. To explore this possibility, we have created continuous, compositionally graded Ti–Al thin films by sputtering and have used nanoindentation to quickly assess the mechanical properties of these alloys as a function of composition. This paper constitutes a first report on this effort.

Our combinatorial approach involves measuring thin film mechanical properties as a function of composition and microstructure and using those measurements to track the properties of bulk structural alloys. The prospective validity of this approach requires some explanation. It is well known that thin films are much stronger than bulk materials [11,12]. Thin films differ from the bulk in the size scale of the microstructure; the thin films have smaller grain sizes, and the film thickness itself will lead to higher strengths when compared with bulk material of the same composition. Hence, the use of thin films to deduce bulk mechanical property trends will be most effective when the strengthening mechanism is microstructure independent, for example in cases where there is a phase transition or a compositional dependence of hardness. As the mechanical properties are scanned through various compositions across a phase diagram, our method is expected to show the differences in mechanical properties of the various phases encountered. Thus, an alloy system, Ti–Al, with phases having considerably different mechanical properties was chosen for our study.

2. Experimental

2.1. Combinatorial Ti–Al thin film synthesis

Ti–Al alloys are widely used as structural materials for high temperature applications and the properties of this alloy system are of general interest to other researchers engaged in the development of materials for automotive and gas turbine engines. These developments allow us to have prior knowledge of the mechanical strengths of Ti–Al alloys with which we can compare our results from the combinatorial approach. The Ti–Al alloy system is fit for our study because there is a softer α-Ti region in the low Al content range and a stronger Ti3Al intermetallic phase at higher Al contents. Thus, we have chosen to explore the portion of the Ti–Al binary alloy system corresponding to 0–35 at.% Al, where our aim is to probe the differences in mechanical strength that are revealed as we scan through the softer α-Ti phase to the stronger Ti3Al intermetallic phase.

We have successfully created alloy films of nearly uniform thickness with compositions that vary approximately linearly across the film using sputter deposition, using sputter deposition from a UHV system with four-targets in a confocal geometry (Fig. 1). The guns are 90° apart from each other, and the angle between the substrate normal and the line joining the center of the target to the center of the substrate is 35° for the target to substrate distance of 6.7 in. used for our experiments. By fixing the flux coming from the three Ti sources and varying the flux from the Al source, we have produced a series of compositionally graded Ti–Al thin films with different average Al concentrations. An average power of 105 W was used with the three Ti guns to achieve a deposition rate of 0.44 Å/s per gun, and the power from the Al gun was varied in the range of 16–47 W to achieve deposition rate of 0.14–0.43 Å/s. We have deposited 1 µm thick Ti–Al thin films onto (100)Si substrates at 500 °C to achieve fully ordered structures; a diffusion barrier of ~150 nm of silicon nitride layer between the Si substrate and the Ti–Al film was used to avoid silicide formation at high
temperatures. The base pressure was $\sim 10^{-9}$ Torr and the Ar pressure during deposition was 3 mTorr.

The prepared Ti–Al thin film samples were characterized in various ways. We first used SEM energy dispersive spectrum (EDS) measurements to determine the composition gradients (Fig. 2). A 15 kV electron beam was used to acquire data from deep enough in the film to obtain an average composition through the depth of the film. As shown in the plot of composition vs. position (Fig. 2), we were able to confirm that our deposition approach produces the linear composition gradients that we had sought. The sample with a center composition of Ti–15 at.% Al was also analyzed with microprobe and those results are included in Fig. 2. The microprobe results showed the same trend, although the absolute values are slightly lower compared to the measurements made with SEM-EDS.

Ti–Al alloy system is known to form metastable super-saturated $\alpha$-Ti instead of forming the stable phase of Ti$_3$Al [13]. For our experiments, the substrate was held at high temperature of 500 °C during deposition to avoid formation of this metastable phase. To confirm the presence of the equilibrium phases at various compositions, TEM selected area diffraction (SAD) patterns were studied from plan-view specimens. One sample was prepared for each of the stable phase regions indicated by the phase diagram ($\alpha$-Ti single phase, $\alpha$-Ti + Ti$_3$Al two phase, and Ti$_3$Al single phase), and selected area diffraction experiments were performed on each specimen (Fig. 3). The SAD ring pattern of the sample from the $\alpha$-Ti region corresponded to that of the $\alpha$-Ti structure, while the SAD pattern of the Ti$_3$Al region showed two extra rings, (101) and (110), that could only correspond to the ordered intermetallic Ti$_3$Al structure and not the $\alpha$-Ti solid solution structure. The SAD pattern taken from the two-phase regions showed a decrease in intensity of the Ti$_3$Al (101) ring with decrease in Al composition, and this agrees favorably with the fact that there should be less Ti$_3$Al phase with decreasing Al content. The presence of equilibrium phases were thus confirmed, which allowed our combinatorial study to explore the mechanical properties of only the stable phases that appear in the phase diagram.

The microprobe analysis of the film with a center composition of 15 at.% Al was performed at varying beam energies of 9, 12, 15 kV to obtain thickness information about the Ti–Al thin film. The calculated thickness profile is shown in Fig. 4, and it confirms the thickness uniformity with the given sputtering configuration. The film is about 10% thinner at the edges compared to the center.

2.2. Nanoindentation of compositionally graded Ti–Al thin films

Ti–Al thin films with graded compositions were tested using a nanoindenter to obtain mechanical
properties as a function of composition. The Nano XP™
(MTS Nano Innovation Center, Oak Ridge, TN) with a
Berkovich diamond indenter tip was operated in the
continuous stiffness mode (CSM) at a constant strain
rate \( \dot{\varepsilon} = P \) of 0.05 s\(^{-1}\) to continuously measure the
indentation depth, load, and stiffness. The samples were
indented at various points along the length of the wafer,
where the aluminum content continuously varies, and
the reported properties are from an average of \( \sim 25 \) in-
dents spaced 50 \( \mu \)m apart at each location. The indentations
were made up to a depth corresponding to the
thickness of the film (1 \( \mu \)m), although, as discussed be-
low, the properties of the film are extracted from the
data at shallow depths.

3. Results and discussion

3.1. Interpretation of the nanoindentation results from
film/substrate systems

3.1.1. Oliver & Pharr hardness

The most well-established technique for analyzing
nanoindentation data is the Oliver & Pharr method,
which is based on a calibrated contact area function,
\( A_c(h) \), for the indenter tip determined from indenting a
sample of known elastic modulus, usually fused silica.
In the Oliver & Pharr model, the hardness is then deter-
mined by

\[
H(O&P) = \frac{P}{A_c},
\]

where \( P \) is the load on the sample and \( A_c \) is the cali-
brated area function [14].

We first used the Oliver & Pharr model to evaluate the
hardness of the combinatorially deposited Ti–Al al-
loy thin films. An example of the resulting hardness,
\( H(O&P) \), vs. indentation depth is shown in Fig. 5. The
\( H(O&P) \) rises continuously with indentation depth, sug-
suggesting that either pile-up\(^1\) or substrate effects may be affecting the indentation response. Nevertheless, the averaged Oliver & Pharr hardness at an indentation depth of 200 nm was determined from the array of indentations at each location and these properties were correlated with the composition data from EDS through a plot of \(H\) (O&P) as a function of composition, as shown in Fig. 6. The error bars indicate a spread in the calculated hardnesses of the array of indentations at each location. A significant amount of uncertainty in the hardness is found using the standard Oliver & Pharr method. The Oliver & Pharr method of analysis relies heavily on an accurate determination of the contact area through the calibration process, and it does not incorporate the effects of indentation shape (pile-up, sink-in) or the elastic mismatch effects caused by the substrate; the Oliver & Pharr analysis method yields the combined properties of the film and the substrate. Thus, a new method for extracting the properties of the film only is needed to further investigate the possibility of using nanoindentation to probe the mechanical properties of combinatorially deposited thin films.

In the case of pile-up, the contact area determined from the calibrated area function is smaller than the actual contact area, and the \(H\) (O&P) would overestimate the real hardness.

3.1.2. Pile-up observations

To show that pile-up is at least partially responsible for the rise in hardness with increasing indentation depth and for the scatter in the Oliver & Pharr hardness, we sought to directly observe pile-up around the indentations. A series of indentations of varying size were made, and their shapes were scanned using an AFM and/or the Nano XP Nanostage. Pile-up was observed for indentation depths greater than 300–500 nm. An AFM scan of an indent 300 nm deep is shown in Fig. 7, and the cross-sectional profile shows a pile-up height of 79 nm. For 200 nm indents, however, it was difficult to observe pile-up due to the inherent roughness of the Ti–Al thin films sputtered at 500 °C. The presence of pile-up during indentation leads to errors in the contact area using the Oliver & Pharr method. Thus a new method of analysis designed to minimize the errors associated with pile-up is needed.

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\(^{1}\) Pile-up: material is pushed against the sides of the indenter tip.
3.2. A new method for determining the hardness of a thin film on a substrate

As discussed above, there are at least two factors that may be contributing to the increase in hardness with increasing indentation depth: pile-up and the elastic modulus mismatch between the film and substrate. Here, we consider each of these effects in turn and develop a method to correct for them.

To minimize errors in the contact area associated with surface roughness and/or pile-up/sink-in that can arise when the Oliver & Pharr method is used, Joslin and Oliver [15] suggested a new method of analysis based on a measurement of the contact stiffness. They noted that the contact stiffness gives a direct measure of the contact area, provided the elastic properties are known. By eliminating the contact area from the following relations:

\[
S = \beta \frac{2}{\sqrt{\pi}} E_s \sqrt{A_c},
\]

\[
H = \frac{P}{A_c},
\]

they showed that the hardness could be expressed as

\[
\frac{H}{E_i^2} = \beta^2 \frac{4}{\pi} \frac{P}{S^2},
\]

where \( H \) is the hardness, \( E_i \) is the reduced modulus, \( P \) is the load, and \( S \) is the contact stiffness. The contact area, \( A_c \), is not included in Eq. (4) and is not needed in this approach. Instead, the hardness is determined by measuring \( P/S^2 \) and using the known modulus to determine the hardness; this procedure minimizes errors associated with uncertainties in the contact area. A limitation of the Joslin & Oliver method, however, is that the method applies only to monolithic, homogeneous materials. Thus an extension of this method is needed for elastically mismatched film/substrate systems.

For the case of elastically inhomogeneous film/substrate systems, we extend the Joslin & Oliver method as follows. We re-arrange Eq. (4) to write

\[
H = \frac{P}{A_c} = \beta^2 \frac{4}{\pi} \frac{P}{S^2} E_i^2,
\]

where \( H \) is the hardness of the film and \( E_i \) is the reduced modulus for the film/substrate system. Below we describe the method of analysis used to determine \( E_i \) for use in determining the film hardness.

Early attempts to model the indentation behavior of films on substrates involved developing a model for the reduced modulus for a film/substrate structure as a function of indentation depth [16–18]. In particular, Saha and Nix [16] modified King’s numerical solution [18] for a flat-ended triangular punch elastically indenting a flat film on an elastic half-space to estimate the reduced modulus for elastic–plastic indentation of a film/substrate system. Their analysis led to following formula for the reduced modulus:

\[
\frac{1}{E_r} = \frac{(1-v_s^2)}{E_s} + \frac{(1-v_f^2)}{E_f} \left( 1 - e^{-t^2/h^2} \right) + \frac{(1-v_s^2)}{E_s} \left( e^{-t^2/h^2} \right),
\]

where \( E_s \) and \( E_f \) are Young’s moduli for the substrate and film, respectively; \( v_s \) and \( v_f \) are Poisson’s ratio for the substrate and film, respectively; \( a = \sqrt{A_c} \); \( t \) is the thickness of the film; \( h \) is the indentation depth; and \( \beta \) is a numerically determined scaling parameter which is a function of \( alt \) (the normalized punch size) that is different for different indenter tip geometries. In the model used by Saha and Nix [16], the Berkovich indenter tip penetrating the film is assumed to be elastically equivalent to a flat punch indenting a film of reduced thickness, \( t - h \). Saha and Nix compared the reduced modulus given by this model with experimental data for Al thin films on glass, sapphire, Si and Al substrates and concluded that the calculated \( E_i \) matches the experimental data reasonably well for indentation depths less than 50% of the film thickness.

Using the re-arranged Joslin & Oliver equation (Eq. (5)), and the reduced modulus given by Saha and Nix (Eq. (6)), we propose a new method for extracting the film hardness from nanoindentation experiments.
on film/substrate systems. We first calculate the reduced modulus, $E_r$, as a function of indentation depth using the Saha and Nix model and then use Eq. (5) from Joslin & Oliver, $H = \frac{E}{2(1+\nu)} = \frac{\beta^2 L^2 E^3}{n^2 S^2}$, to obtain the hardness of the film as a function of indentation depth. This method of determining the hardness eliminates some of the errors associated with pile-up and elastic mismatch. A plot of hardness vs. indentation depth would be expected to show a distinct “plateau” region at shallow indentation depths where the hardness is essentially independent of indentation depth.

In the limit where the depth of indentation is just equal to the film thickness, the reduced modulus given by the Saha and Nix formula reduces to that for the substrate since the model assumes a flat-ended indenter acting on the substrate alone at that point. However, in the nanoindentation experiments, the sides of the Berkovich indenter are still in contact with the film material when the very tip reaches the film/substrate interface. This is the reason the Saha–Nix model greatly overestimates the influence of the substrate at very large indentation depths. Thus, the model of Saha and Nix is not valid beyond 50% of the film thickness, and the described “plateau” from above would not be expected to extend beyond that indentation depth. As shown in Fig. 8, a distinct plateau in the hardness vs. depth curve is not observed at shallow depths even after the corrections described here have been made. We must conclude that the corrections we have made do not account for all of the factors affecting the hardness of the film. Thus, we choose to determine the hardness at an indentation depth at a particular fraction of the film thickness. Because the corrections we are making for the elastic mismatch are expected to be good to a depth of 50% of the film thickness, and since we wish to avoid severe surface roughness effects, we take 20% of the film thickness for these measurements. We call this the hardness of the film or, sometimes, the corrected hardness, to distinguish it from the Oliver & Pharr hardness. Using this procedure the film properties can be estimated as a function of composition.

Both the Oliver & Pharr hardness, $H(O&P)$, and the corrected hardness, $H_r$, of a 1 μm thick Ti–25at.%Al thin film are plotted as a function of the indentation depth in Fig. 8. Even in the early stages of indentation, the Oliver & Pharr hardness is greater than the corrected hardness, suggesting the possibility of pile-up. When pile-up occurs, the contact area is underestimated in the Oliver & Pharr method, and $H(O&P)$ values are overestimated. As shown in the figure, by using the calculated reduced modulus of Saha and Nix together with the measured contact stiffnesses, we are able to remove some of the errors in the contact area and thus obtain a better estimate of the true hardness of the thin film.

The hardnesses of the Ti–Al thin films calculated using this new method (values taken at 20%* $t_f = 200$ nm) are shown in Fig. 9. A comparison of Fig. 9 with the plot of Oliver & Pharr hardness shown in Fig. 6 shows that the uncertainty associated with incorrect estimates of the contact area are significantly reduced by the new method of analysis.

If all of the difference between the Oliver & Pharr hardness and the corrected hardness shown in Fig. 8 were caused by pile-up, then an observable pile-up around the indentation should be observed, even for an indentation depth as small as 200 nm. A simple calculation based on the observed differences in hardness...
leads to an estimate of \( \sim 96 \) nm for the pile-up at an indentation depth of 300 nm, which is smaller than but comparable to the pile-up of 79 nm shown in the AFM scan in Fig. 7. As explained above, it was difficult to observe pile-up at an indentation depth of 200 nm due to the inherent roughness of the Ti–Al thin films sputtered at 500°C. The estimated calculation of pile-up height at 200 nm is \( \sim 70 \) nm for the same sample.

3.3. Capability of the thin film combinatorial method for estimating bulk properties

With the improvements in determining the properties of thin films on substrates using our new method, more accurate measurements of the hardneses were possible. The overall purpose of the combinatorial approach is to identify compositions of interest that might subsequently merit development as bulk structural materials. For this approach to have merit, the properties surveyed by nanoindentation should correlate strongly with the properties of bulk structural alloys. In Fig. 10, the hardneses of various compositions are plotted together with the estimated hardness of the bulk Ti–Al alloy \( (H \sim 3\sigma_{YS}) \) [19–21]. The measured thin film hardness in the \( \alpha \)-Ti region starts at \( \sim 3 \) GPa rises approximately linearly across the two-phase region, and reaches \( \sim 4.5 \) GPa in the intermetallic Ti₃Al region, as expected. Also as expected, the hardneses of our thin films are generally higher than those of the bulk alloys because of both indentation size effects [11,12] and the differences in thin film microstructure compared with the bulk microstructure. Although the magnitude of the observed hardneses are different, the general trends obtained from the thin film measurements, however, closely track the properties of bulk alloys. While the microstructures of thin films differ significantly from those of bulk materials, the similarity of the trends in hardness with composition suggests that the present combinatorial method captures the composition and phase dependence of the mechanical properties of this alloy. Thus, the feasibility of using the thin film combinatorial method to estimate bulk properties is verified. Rodriguez and Gutierrez [11] showed that the bulk properties of several finely structured alloys could be predicted using nanoindentation, provided that the indentation size effect is taken into account. We expect that such methods could be used to bring the nanoindentation data for thin films into closer absolute agreement with bulk properties.

4. Summary

We have developed a combinatorial method for identifying alloy compositions of potential interest as structural materials. By sputter depositing Ti–Al alloy thin films with linearly graded compositions and using nanoindentation to quickly scan through the mechanical properties of the composition “library”, we are able to track the changing mechanical properties with composition. We have developed a new method for extracting film properties from indentation experiments on film/substrate systems, based on a direct measurement of the contact stiffness and a calculation of the reduced modulus. Application of the new method to the combinatorial Ti–Al thin films showed a significant reduction in scatter/error in hardness compared to that of the Oliver & Pharr method, minimizing errors in the contact area associated with pile-up and elastic modulus mismatch. The corrected hardness of the Ti–Al alloy thin films correlated well with the composition and successfully tracked the bulk properties of this alloy. Our results showed the expected trend of lower hardness in \( \alpha \)-Ti region, linearly increasing hardness in the two-phase region, and higher hardness for the stronger Ti₃Al intermetallic. We conclude that the combinatorial method may be an efficient technique for quickly scanning through various compositions of structural alloys to identify compositions of interest for further development.

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