DETERMINATION OF ACTIVATION ENERGY OF INTERMIXING
IN TEXTURED METAL-METAL MULTILAYER FILMS
VIA TWO-DIMENSIONAL X-RAY DIFFRACTION

Mark A. Rodriguez, David P. Adams, and Ralph G. Tissot
Sandia National Laboratories, Albuquerque, NM 87185-1411

ABSTRACT

Activation energies for the intermixing reaction of textured metal-metal multilayer thin films have been determined using x-ray diffraction analysis. Kinetic data were collected utilizing an area detector so as to reduce intensity bias from changes in out-of-plane texture during the intermixing reaction. Activation energies for Al/Pt, Ni/Ti, and Co/Al metal-metal multilayer thin films have been determined as 95.4(2) kJ/mol, 201(13) kJ/mol, and 247(19) kJ/mol, respectively.

INTRODUCTION

Multilayer thin films show great potential as mirrors, strong and tough coatings, heat sources for alternative joining processes, and other applications.[1-7] Often these films have periodicities that are much less than 1.0 μm, yet are constructed to have hundreds or thousands of individual layers with minimal intermixing. Figure 1 shows a cross-section Transmission Electron Microscopy (TEM) image of a Ni/Ti multilayer. As shown, this multilayer film has a well-defined periodicity and a large number of metal layers; in this case composed of elemental Ni and Ti. The bilayer thickness (τBL) for the Ni/Ti film shown in Figure 1 is 670 Å where τBL is defined as the sum of the two individual layers of each deposited element.

One issue concerning nanometer-scaled multilayers is the deterioration of multilayer periodicity and compositional modulation over long times at relatively low temperatures.[8] Since the species can react to form intermetallics compounds, small temperature increases can result in an intermixing reaction that ultimately affects performance. One of our goals has been to quantify the intermixing reaction behavior to garner a better understanding of storage shelf-life for various films. Results of activation energy determination via High Temperature X-Ray Diffraction (HTXRD) analysis are presented. Our analysis employs the use of an area detector to address potential biasing of data due to texture decay during ‘loss’ of a reactant. This was deemed necessary because as the film reacts, the texture decays along with the reactant concentration. The use of the area detector aids in the true intensity decay determination through the summation of the textured peak profiles in the χ angle dimension (in-plane tilting), thus removing the potential error associated with 1D detector analysis.
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

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EXPERIMENTAL

Synthesis of Multilayer Films

Multilayers were fabricated using direct-current sputtering employing a Unifilm deposition apparatus (Unifilm, Boulder, CO). The system was cryopumped to a base pressure of $8 \times 10^{-8}$ Torr prior to deposition. Argon sputtering gas (10 mTorr) was utilized during the sputtering process. Films were deposited on 0.5 mm thick fused silica substrates (Meller Optics, Providence, RI) where the substrate temperature remained less than 50°C throughout the deposition process. High purity sputter targets were employed: Al (99.995%), Pt (99.95%), Ni (99.99%), Ti (99.99%), and Co (99.99%). Fabricated Al/Pt bilayers were 400 Å thick (Al ~200 Å; Pt ~200 Å) with a total of 5 bilayers (overall thickness ~ 0.2 µm). In the case of Co/Al and Ni/Ti bilayers, the thickness was increased to ~500 Å bilayers with a total of 20 bilayers (total thickness ~1 µm). Ni/Ti and Co/Al films required additional thickness as compared to the Al/Pt films to improve overall scattered intensity of the constituent phases.

XRD Data Collection

Diffraction measurements were performed using a Bruker D8 Discover system equipped with a High-Star area detector and an Anton-Parr DHS 900 hot-stage. The deposited samples were first diced into ~1 cm square pieces. These pieces were individually loaded onto the hot-stage and held in place via small metal clips, which pressed the specimen against the Inconel heating block. The hot-stage was equipped with a Mylar dome which can be placed over the sample during heating. Vacuum conditions (~2 x $10^{-3}$ Torr) were obtained within the Mylar dome environment through the use of a roughing pump attached to the hot-stage plumbing. This was done to reduce the possible oxidation of the multilayer films during heating. Reaction rate data were collected at various temperatures between 80-350°C. Films were all heated using a 10°C
heating rate to the set point temperature. A 2°C overshoot was typical for the heating stage. The stage equilibrated within 1-2 minutes of achieving the set point temperature. The temperature was calibrated based on the thermal expansion of Alumina and was verified by the use of independent property measurements of the films (i.e. DSC).

For each bilayer film sample, initial X-ray diffraction scans were performed to identify the presence of, and out-of-plane texture associated with, the deposited multilayers. Our selection of the hkl to be monitored for kinetic data was based on these initial scans. For the case of Al/Pt films the Pt (111) peak was selected. For Ni/Ti films the Ni (111) peak was chosen; the Al (111) peak was used for the Al/Co films. The selected reflection was centered in the area detector and θ was fixed at half the 2θ angle to obtain a symmetrical geometry. For the case of the Al/Pt (111) peak, the entire Pt (111) textured intensity fit within the frame. Integration of the Pt (111) intensity was straightforward as the total intensity could be encompassed by a conic with width of 2° 2θ and ±20° in χ angle as shown in Figure 2. Also shown in Figure 2 is a decay curve of Pt concentration based on integrated peak area of the Pt (111) reflection. This plot shows three distinct regions based on the observed slope of the line. These regions will be discussed in more detail later.

Figure 2. Left: area detector frame from Al/Pt multilayer showing textured Pt (111) peak. Right: rate data obtained from intensity decay of Pt (111) peak which show three regions: (i) temperature overshoot; (ii.) region of linear decay; (iii.) slowed intermixing.

In the case of the Ni/Ti and Co/Al multilayers, the intensity distribution exceeded the frame size. Therefore, the film was tilted by 30° in χ so that only one side of the discontinuous Debye cone was visible. In this way, it was possible to integrate at least half of the textured intensity, and thereby monitor the textured intensity during the intermixing reaction. Figure 3 illustrates how the specimen was oriented and the resulting frame appearance for the Ni (111) peak on a Ni/Ti multilayer, and the intensity decay with time for both the Ni (111) and Ti (002) reflections. Integrated peaks were generated via the General Area Detector Diffraction System (GADDS) software.[9] These peaks represented the summed intensity of the selected reflection in both χ.
and 2θ. These peaks were subsequently profile-fit using JADE software.[10] The relative intensity as a function of time was determined based on the integrated area of the profiles.

Figure 3. Left: frame image from Ni/Ti film showing integrated section of partial Debye ring. Top Right: orientation of film relative to incident beam. Bottom Right: intensity decay with time at constant temperature (290°C).

RESULTS AND DISCUSSION

As discussed earlier, Figure 2 shows three distinct regions within the rate plot for Pt (111) at 110°C. This graph is typical of our results for all multilayers. Region (i) of the plot shows a steep drop of intensity, followed by (ii) a relatively linear range of decay which is then concluded by (iii) a slower intermixing behavior. The initial fast slope (i) for the peak intensity decay is likely due to the temperature overshoot upon nearing the set point of the heater. This was consistently observed for all the films analyzed and the duration coincided with the transient timeframe where the temperature exceeded the set point. Region (ii) occurred once the set point temperature stabilized. Finally, region (iii) is demarcated by a clear break in the slope after significant reaction time and is indicative of the slowing of the intermixing reaction, likely due to impeded diffusion. We employed region (ii) to perform our determination of the rate constant for a given temperature. Our analysis assumes a pseudo first-order reaction behavior of the film.[11] This assumption appears to work well for the limited range of linearity selected for rate constant determination, and serves us well for the monitoring of only one constituent in the intermixing reaction. Concentration of constituent reactants was assumed to be proportional to the integrated intensity of the discontinuous Debye ring for the monitored peak. Rate constants were determined for at least three films at various temperatures for each multilayer film pairing. Table 1 lists the measured rate constants and temperatures for each multilayer measured.
Table 1. Measured rate constants for various metal-metal multilayers.

<table>
<thead>
<tr>
<th></th>
<th>Al/Pt</th>
<th>Ni/Ti</th>
<th>Co/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>k (s⁻¹)</td>
<td>T (°C)</td>
<td>k (s⁻¹)</td>
</tr>
<tr>
<td>80</td>
<td>1.07x10⁻⁵</td>
<td>270</td>
<td>3.3x10⁻³</td>
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<tr>
<td>90</td>
<td>2.66x10⁻⁵</td>
<td>280</td>
<td>7.7x10⁻⁵</td>
</tr>
<tr>
<td>110</td>
<td>1.27x10⁻⁴</td>
<td>290</td>
<td>1.4x10⁻⁴</td>
</tr>
<tr>
<td>120</td>
<td>3.08x10⁻⁴</td>
<td>300</td>
<td>3.6x10⁻⁴</td>
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<td></td>
<td>170</td>
<td>180</td>
<td>190</td>
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<tr>
<td></td>
<td>8.56x10⁻⁵</td>
<td>3.11x10⁻⁴</td>
<td>1.55x10⁻³</td>
</tr>
</tbody>
</table>

Rate constants were plotted using the conventional Arrhenius plot as shown in Figure 4. These data were employed to determine the activation energy values for the intermixing reaction for the multilayers. When evaluating Figure 4, one can see that the slope characteristic of the Al/Pt is much shallower as compared to that of the Ni/Ti and Co/Al. This is reflected in the determined activation energies, showing the Al/Pt films having less than half the activation energy for intermixing as compared to the Co/Al and Ni/Ti films (see Table 2). Prefactor values for the Arrhenius fits are also listed in Table 2. While these are difficult to interpret in terms of collision theory[11], it is clear that there is a strong variability between these values for the differing multilayer systems. Al/Pt shows the smallest exponential prefactor value, which likely reflects the shallow slope of the Arrhenius plot.

![Figure 4. Arrhenius plot of reaction rate data for various metal-metal multilayers.](image-url)
Table 2. Summary of activation energies for various metal-metal multilayers.

<table>
<thead>
<tr>
<th>Film</th>
<th>Bilayer Thickness (Å)</th>
<th>Number of Bilayers</th>
<th>Total thickness (µm)</th>
<th>Observed hk/λ</th>
<th>Activation Energy/ E_a (kJ/mol)</th>
<th>Prefactor / A (mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Pt</td>
<td>400</td>
<td>5</td>
<td>0.20</td>
<td>Pt (111)</td>
<td>95.4(2)</td>
<td>1.4×10⁹</td>
</tr>
<tr>
<td>Ni/Ti</td>
<td>522</td>
<td>20</td>
<td>1.04</td>
<td>Ni (111)</td>
<td>201(13)</td>
<td>5.8×10¹⁴</td>
</tr>
<tr>
<td>Co/Al</td>
<td>500</td>
<td>20</td>
<td>1.00</td>
<td>Al (111)</td>
<td>247(19)</td>
<td>1.1×10²⁵</td>
</tr>
</tbody>
</table>

CONCLUSION

Activation energies have been determined for textured Al/Pt, Ni/Ti, and Co/Al metal-metal multilayers. Results indicate that the activation energy for the intermixing reaction of Al/Pt multilayers is less than half the energy as compared to Ni/Ti and Co/Al films. This suggests higher intermixing behavior and hence, significantly shorter shelf-life for Al/Pt multilayers.

ACKNOWLEDGMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000. We would like to acknowledge Luke Brewer (Sandia) for collection of cross-sectional TEM micrographs of Ni/Ti multilayers.

REFERENCES

9. GADDS (ver. 4.1.23), Bruker-AXS, Inc. Madison, WI.
10. JADE (ver. 8.5.2), Materials Data, Inc. Livermore, CA.