ALUMINUM/COPPER NANOCOMPOSITES FABRICATED BY THE JET VAPOR DEPOSITION™ PROCESS


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ABSTRACT

Aluminum and copper nanolaminates have been fabricated at Jet Process Corporation using the novel, proprietary Jet Vapor Deposition™ (JVD)™ process. Laminates with a total thickness of 10 μm were made by depositing alternating layers of approximately equal thicknesses of copper and aluminum onto preheated silicon wafers at a substrate temperature of ~140 °C. The layer thicknesses were systematically varied between 20 nm and 1 μm. The microstructure and properties of the laminates were investigated using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and nanoindentation methods. TEM has shown that the laminates have a strong [111] texture. The hardness results show that above a critical layer thickness of approximately 50 nm, the yield strength of the composites varies inversely with the layer thickness, while the strength of nanolaminates with layer thicknesses smaller than the critical thickness is better explained by the Koehler model. An alternative model recently proposed by Embury and Hirth fits the data equally well.

INTRODUCTION

Novel vapor phase synthesis methods are beginning to emerge with the capability of creating affordable composite structures with independently controlled volume fractions and thickness of two or more constituents [1, 2]. They offer the opportunity to synthesize lamellar composites with nanometer scale dimensions and to vary the layer type and spacing throughout the composite's thickness, thus creating graded microstructure materials. Here, we explore the use of the novel, proprietary Jet Vapor Deposition™ (JVD)™ process developed by Jet Process Corporation, New Haven, CT [3, 4, 5, 6]. The JVD process uses sonic, high purity helium (He) and hydrogen (H₂) gas jets to entrain atomically dispersed vapor and deposit films/coatings. It is of interest here because several jets can be used sequentially to deposit multilayered materials inexpensively and at high rates. Its potential value for this is examined by depositing and measuring the strength of a model metal-metal system.

Background and Theory

Materials with thin, multilayered structures are of interest because they potentially offer novel mechanical and physical properties [7, 8]. The movement of dislocations in these structures has been an area of growing interest [9]. Koehler used an image force model to analyze the strength of layered materials of very thin layer thicknesses [10]. He predicted that if one of the layer constituents had a significantly lower shear modulus than the other, dislocations would have to overcome a large repulsive image force in order to move from metal layer B of lower shear modulus...
(\mu_B) into the A metal layer (with shear modulus \mu_A > \mu_B). This image force (F) is given approximately by:

\[ F = \frac{R \mu_B b^2 \sin \theta}{4\pi} \]  

where \( R = (\mu_A - \mu_B)/(\mu_A + \mu_B) \), \( b \) is the magnitude of Burgers vector in metal layer B, \( \theta \) is the angle between the A/B metal interface and the slip plane, and \( r \) is the distance between the dislocation and the nearest interface. Equation (1) indicates the image force is proportional to the difference in shear moduli for the two metal layers and rapidly increases as the dislocation approaches the interface. The maximum stress (\( \sigma_m = F/b \)) will be reached when the dislocation reaches the interface, i.e., when \( r \) is approximately equal to the radius of a dislocation core (\( \pm 2b \)). In this case \( \sigma_m = R \mu_B \sin \theta/8\pi \) and is independent of the B layer thickness (\( \lambda_B \)). When Koehler's mechanism controls yielding and if isostress conditions are assumed to apply, application of a rule-of-mixtures model to the yield stress of a multilayer sample with equal A and B layer thicknesses gives:

\[ \sigma_y = R \mu_B \sin \theta \left(1 + \frac{E_A}{E_B}\right)/16\pi m \]  

where \( E_A \) and \( E_B \) are Young's moduli of A and B, respectively, and \( m \) is the Schmid factor for the operative slip system. Again, this is independent of the layer thickness. For different A, B layer thicknesses, the yield strength under isostress conditions would be:

\[ \sigma_y = R \mu_B \sin \theta \left(\frac{\lambda_B}{\lambda_A + \lambda_B} + \frac{\lambda_A}{\lambda_A + \lambda_B} \left(\frac{E_A}{E_B}\right)\right)/8\pi m \]  

where \( \lambda_A \) and \( \lambda_B \) are the layer thicknesses of A and B, respectively.

Lehoczky experimentally demonstrated that the yield strength of Al/Cu multilayers with equal Al and Cu layer thicknesses conformed to the Koehler model when the layer spacing was below a critical value of \( \approx 70 \) nm [11]. However, when the layer thickness was greater than \( \approx 70 \) nm, the strength was better fitted to a Hall-Petch type relation:

\[ \sigma_y = \sigma^* + k \lambda_B^{-n} \]  

where \( \sigma^* \) is a frictional stress, \( k \) is a constant, \( n \) lies between 0.5 and 1, and \( \lambda_B \) is the B layer thickness. These results suggest that an Orowan or Frank-Read type of mechanism operates in the Al/Cu multilayers and governs yielding for \( \lambda_B > 70 \) nm. In this regime, \( \sigma_y \) is strongly dependent on the metal layer thickness. However, Koehler's mechanism only controls yielding when the metal layer is so thin that Frank-Read and/or Orowan mechanisms are not operative in either layer. In this situation, the movement of dislocations towards and into the interface would presumably be the only mechanism by which plastic deformation could occur.

To estimate the strength in this case, suppose a slip plane within metal layer B is inclined to the A/B interfaces at an angle and intercepts the interfaces at P and Q [Fig. 1(a)]. The plan view of the slip plane with a single dislocation loop is shown in Fig. 1(b). The dislocation loop is confined in a very small space (\( \lambda_B/\sin \theta \)) between two A/B interfaces with two dislocation segments pinned along the A/B interfaces, and the rest of the loop is movable in the slip plane. The movable dislocation segments can be viewed as Orowan dislocations. The critical resolved shear stress (\( \tau_P \)) required to move the Orowan dislocations is:
\[ \tau_f = \frac{2\alpha \mu_B b \sin \theta}{\lambda_B} \]

where \( \alpha \) is a constant between 0.5 and 1 \([12]\). As \( \lambda_B \) is decreased, \( \tau_f \) increases. For \( \lambda_B \) less than a critical thickness, \( \tau_f \) eventually exceeds the maximum image stress (\( \tau_m \equiv R\mu_B \sin \theta / \delta \pi \)), and the image force mechanism will then be responsible for yielding. The critical thickness (\( \lambda_c \)) at which this occurs can be found by setting \( \tau_f \) equal to \( \tau_m \) from which:

\[ \lambda_c = \frac{\alpha 16 b}{R} \]

wherein b, \( \alpha \) and R have been previously defined.

Figure 1. Schematic representations of (a) the geometry of a slip plane within a low modulus constituent layer, (b) a dislocation loop confined in a small space between two A/B interfaces with two dislocation segments pinned along the A/B interfaces and the rest of the loop movable in the slip plane.

Thus, multilayers with a metal layer thickness less than a critical thickness, defined by equation (6), are expected to exhibit a different deformation behavior from that observed in any monolithic material or in multilayers with a layer thickness greater than \( \lambda_c \). We also note that according to equation (6), the greater the shear modulus difference (R), the smaller the critical metal thickness for the transition from a Hall-Petch to a Koehler type behavior. Together, equations (2), (3), (5) and (6) suggest that modifying layer spacings and thicknesses will provide great flexibility for independently manipulating many of the mechanical properties such as modulus, strength, and toughness of nanocomposite materials. If they can be shown to be a valid description of the strength-nanostructure relationship, they could be used to design the mesoscale structure gradients of future FGM's.

Synthesis Techniques

If tomorrow's nanocomposite designs are to be realized, inexpensive and flexible approaches for their near-net shape synthesis and processing are needed. There are many potential approaches for fabricating layered nanocomposites. Directionally solidified eutectic reactions have been traditionally used to produce in situ composites with lamellar structures. In particular, Ni/\( \gamma' \)/Al-Ni3Nb (\( \gamma \gamma' \)-5) or Ni3Al-Ni3Nb (\( \gamma' \)-8) lamellar eutectics have been extensively explored [13, 14]. The yield strength of the Ni3Al-Ni3Nb lamellar eutectics obeyed a Hall-Petch type relation. For example, the yield strength increased from \(-750 \) MPa at a 5 \( \mu \)m lamellar spacing to 1.5 GPa at a 1 \( \mu \)m spacing. However, attempts to further increase strength by decreasing the spacing below 1 \( \mu \)m have proven unsuccessful because of the onset of cellular solidification and a consequent loss of the lamellar structure. Other techniques for synthesizing layered materials include...
physical vapor deposition [15, 16, 17, 18] and electrodeposition [19]. Two advanced physical vapor deposition techniques, electron-beam vapor deposition (EBVD) and the JVD process, show particular promise for the synthesis of graded layer nanocomposites because of their potentially high deposition rate (and thus reduced cost) and their multi-material capability.

Alpas et al. recently reported the tensile properties of Al-Al₂O₃ laminar composites deposited at ambient temperature in an EBVD system using a pulsed gas process [17]. The thickness of the aluminum oxide layer was kept constant at ~5 nm, whilst the thickness of the metal Al layer was varied from 50 nm to 500 nm. Only a Hall-Petch type behavior was observed in this case. The yield strength σᵧ increased to a maximum of ~475 MPa when the Al layer thickness decreased to 50 nm, and they fitted their data to a Hall-Petch type equation: σᵧ (MPa) = 27 + 0.1λ⁻¹⁵ (m⁻¹⁵). It is possible that the metal layer thickness was not thin enough to exhibit a Koehler type behavior.

A schematic representation of the JVD process is shown in Fig. 2 [6]. The JVD vapor source is a nozzle incorporated into a "low vacuum" (several hundred Pa), mechanically pumped, fast flow system. High purity helium and/or hydrogen carrier gases emerge from the nozzle as a highly collimated sonic or near sonic jet. Atomic or molecular vapor, generated in the nozzle by evaporation, is entrained in the jet and forms a localized deposit on a downstream substrate. One or more jets can be aimed at a rotating/oscillating substrate carousel. The moving substrates are thereby "scanned" and coated uniformly. Multiple jets operated simultaneously yield alloys, or if operated sequentially, give multilayered composites. Because the JVD process incorporates a fast flow carrier gas and a powerful pumping system, the oxygen residence time in the JVD process deposition chamber is short. Substrate temperatures can also be kept low, therefore avoiding layer interdiffusion. However, when multilayers are deposited at too low a temperature [1, 2], the metal layers tend to be discontinuous. This can be overcome by slightly elevated-temperature deposition [2].

Figure 2. Schematic representation of the Jet Vapor Deposition® process (1 Torr = 133.3 Pa). The deposit vapor is generated near the nozzle exit by mechanisms of thermal vaporization. The dotted arrows indicate substrate motion in two dimensions for large area coverage and uniformity. Ref. [6].
EXPERIMENTAL PROCEDURES

Specimen Preparation

In this study, aluminum-copper multilayers were grown by means of Al and Cu "wire feed" JVD process sources. Both the Al and Cu vapors were created in separated nozzles by feeding aluminum and copper wires under computer control to a resistively-heated (BN-sheathed) tungsten filament. The Al and Cu wire feed rates and carousel rotation frequency were chosen to allow alternating deposition of nanometer dimension Al and aluminum oxide layers at nominal rates of ~1.6 nm/sec over an area of ~12 cm². Silicon wafers with a [111] orientation were used as substrates. The Al/Cu multilayers were ~10 μm thick and had approximately equal thicknesses of Al and Cu. The samples were deposited at a substrate temperature of ~140°C, and the alternating layer thickness was systematically varied from ~20 nm to ~1 μm.

Microstructural Characterization and Hardness Measurement

The microstructure of the as-deposited Al/Cu multilayer samples was examined using a JXA-840A1 scanning electron microscope (SEM) and a Phillips-400T transmission electron microscope (TEM). Both plan-view and cross-sectional TEM specimens were prepared from multilayer samples by standard dimpling and ion-milling procedures. To reduce irradiation damage, ion-milling was performed at 4 V and 0.5 mA at liquid nitrogen temperature.

Hardnesses of the Al/Cu samples were measured at the National Institute of Standards and Technology (NIST) using a nanoindentation technique [20] on a NanoInstruments NanoIndenter II equipped with a triangular pyramid diamond tip. The sides of the pyramid made an angle of 65.3° with the normal to the base of the indenter. The indentations were made at seven different loads ranging from 0.5 mN to 1800 mN in a load control mode. Hardness values were corrected for thermal drift, machine compliance, elastic recovery, and deviation of the indenter tip from perfect Berkovich geometry [20].

RESULTS AND DISCUSSION

Microstructure

Figure 3 shows the distinct multilayered structure of an Al/Cu sample of nominal layer spacing of 1 μm. In the micrograph, the bright contrast layers are copper; those with a darker contrast are aluminum. Figure 4 is a plan-view TEM micrograph showing a typical microstructure observed in an as-deposited Al/Cu multilayer sample with a nominal layer spacing of 100 nm. The appearance of Moiré fringes in Figure 4 suggests that the Al and Cu layers are coherent. A preferred [111] growth direction can be readily seen from the selected-area diffraction (SAD) patterns [Figure 4(a)] generated from the region shown in Figure 4(b). The grain sizes of Al and Cu varied between ~10 nm and ~200 nm. The grain size of the aluminum was usually greater than that of copper. When the interface was carefully examined, fine domains (several nm in lateral size) of a AlCu₃ intermetallic phase were occasionally observed. Since they were extremely small and only occasionally observed, they are presumed to have a minor effect on the strengthening of the multilayers.

1. Certain trade names and products of companies are identified in this paper to adequately specify the materials and equipment used in this research. In no case does such identification imply that the products are necessarily the best available for the purpose or that they are recommended by NIST.
Figure 3. Cross-sectional SEM micrograph showing the layer structure of an Al/Cu nanocomposite with a nominal layer spacing of 1 μm.

(a) Selected-area diffraction patterns generated from the region in (b) showing a preferred (111) growth direction of the multilayer.

(b) Plan-view bright-field (BF) TEM image showing a typical microstructure observed in a Al/Cu multilayer sample (nominal layer spacing of 100 nm).
Hardness and Estimated Yield Strength

Hardness measurements were made on twelve Al/Cu (all deposited at $-140^\circ$C) multilayer samples of each layer thickness. The indentation contact depth $h_c$ (nm), hardness $H$ (GPa), estimated yield strength $\sigma_y$ (MPa), and modulus $E$ (GPa) for each different layer thickness $\lambda_B$ are listed in Table I. The samples were tested at a load of 100 mN.

Table I: Indentation depth, hardness, yield strength and modulus for Al/Cu films tested at a load of 100 mN.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$\lambda_B$ (nm)</th>
<th>$h_c$ (nm)</th>
<th>$H$ (GPa)</th>
<th>$\sigma_y$ (MPa)</th>
<th>$E$ (GPa)</th>
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<tr>
<td>Al</td>
<td>n/a</td>
<td>2667 ± 46</td>
<td>0.56 ± 0.02</td>
<td>187 ± 65</td>
<td>58.6 ± 1.2</td>
</tr>
<tr>
<td>Cu</td>
<td>n/a</td>
<td>1750 ± 13</td>
<td>1.30 ± 0.02</td>
<td>432 ± 6</td>
<td>101.4 ± 1.4</td>
</tr>
<tr>
<td>1</td>
<td>1000</td>
<td>1607 ± 30</td>
<td>1.54 ± 0.06</td>
<td>512 ± 19</td>
<td>118.4 ± 2.5</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>1588 ± 38</td>
<td>1.58 ± 0.08</td>
<td>526 ± 26</td>
<td>98.7 ± 3.6</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>1305 ± 19</td>
<td>2.32 ± 0.06</td>
<td>772 ± 21</td>
<td>113.2 ± 1.8</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>1264 ± 39</td>
<td>2.47 ± 0.15</td>
<td>825 ± 50</td>
<td>114.1 ± 3.6</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>1228 ± 73</td>
<td>2.64 ± 0.30</td>
<td>879 ± 99</td>
<td>110.8 ± 8.3</td>
</tr>
<tr>
<td>6</td>
<td>70</td>
<td>1164 ± 31</td>
<td>2.90 ± 0.14</td>
<td>968 ± 48</td>
<td>105.7 ± 3.1</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>1238 ± 27</td>
<td>2.56 ± 0.12</td>
<td>854 ± 38</td>
<td>105.2 ± 6.3</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>1126 ± 71</td>
<td>3.12 ± 0.36</td>
<td>1039 ± 121</td>
<td>110.9 ± 11.3</td>
</tr>
<tr>
<td>9</td>
<td>40</td>
<td>1213 ± 74</td>
<td>2.70 ± 0.33</td>
<td>901 ± 110</td>
<td>93.2 ± 6.0</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>1287 ± 5</td>
<td>2.38 ± 0.02</td>
<td>793 ± 6</td>
<td>82.4 ± 3.1</td>
</tr>
<tr>
<td>11</td>
<td>25</td>
<td>1020 ± 45</td>
<td>3.76 ± 0.30</td>
<td>1255 ± 100</td>
<td>103.6 ± 6.0</td>
</tr>
<tr>
<td>12</td>
<td>20</td>
<td>1189 ± 67</td>
<td>2.80 ± 0.29</td>
<td>933 ± 98</td>
<td>100.1 ± 8.1</td>
</tr>
</tbody>
</table>

The average contact depths of the 100 mN load indentations for the Al/Cu laminate samples decreased from 1607 ± 30 nm to 1189 ± 67 nm when the nominal layer spacing decreased from 1 μm to 20 nm. This corresponded to an average hardness ($H$) increase from 1.54 ± 0.06 GPa for $\lambda_B = 1$ μm to 2.8 ± 0.29 GPa for $\lambda_B = 20$ nm. These hardness values correspond to estimated yield strengths ($H/3$) of 512 ± 19 MPa and 933 ± 98 MPa, respectively. The measured elastic modulus did not appear to vary significantly with layer thickness. To investigate the yield strength - layer spacing relation for the JVD Al/Cu multilayers, the data points were plotted against the inverse of the layer spacing, Figure 5. The error bars represent one standard deviation of the averaged data points. The results reveal a similar behavior to that reported by Lehoczky on evaporated Al/Cu multilayers [11]: the yield strength appears to be governed by an Orowan mechanism when the layer thickness was greater than a critical thickness of ~50 nm. The best fit was obtained with a $\lambda_B^{-1}$ relation: $\sigma_y$ (MPa) = 538.6 (MPa) + 25375.2 (MPa nm) $\lambda_B^{-1}$ (nm$^{-1}$).
Figure 5. A plot of the yield strength versus the nominal layer spacing of the JVD Al/Cu multilayers. The mean deviation is indicated by vertical bars. The curve fit to a Hall-Petch type relation and the yield strength predicted by a Koehler image force model are also included. The Embury-Hirth model is plotted using a best-fit value for $\lambda$ of 0.44$\lambda_B$ for all samples.

The theoretical yield strength predicted by Koehler's equation (2) is also included in Figure 5. It was assumed that $E_A = 101.4$ GPa (measured by indentation), $E_B = 58.6$ GPa (measured by indentation), $\mu_A = E_A/(1+\nu) = 39.0$ GPa, where $\nu$ ($= 0.3$) is Poisson's ratio, $\mu_B = 22.6$ GPa, $A$ denotes Cu and B denotes Al. Predictions are shown for both equiaxed and [111]-textured ($m = 0.244$) multilayers deforming under isostatic conditions. The estimated yield strength of the JVD Al/Cu samples with alternating layer thickness smaller than ~50 nm is better predicted by a Koehler type relation. The critical layer spacing of ~50 nm for transition from a Hall-Petch to a Koehler type relation is close to the thickness range (depending on $\alpha$) of 26.9 nm ~ 53.8 nm predicted by equation (6), using $b = 0.286$ nm and $R = (\mu_A\mu_B)/\mu_A + \mu_B = 0.266$.

Embrey and Hirth have recently proposed an alternative view of the dislocation mechanism of yielding in multilayered materials [9]. They incorporated the interaction energy of the dislocation with the A - B interface in the Orowan relation. This results in an expression for the shear yield strength of the form:

$$\tau = \frac{2S_c}{b\lambda_B} \ln \left( \frac{\lambda}{2\pi b} \right)$$  \hspace{1cm} (7)

where $\lambda$ is the distance between dislocations and $S_c$ is the edge dislocation interaction energy with the interface boundary. The predicted $\lambda_B$ dependence is plotted on Fig. 5 using a best fit value for $\lambda$ of 0.44$\lambda_B$ for all samples.
Nanocompositing Implications

A possible deposition method for creating layered materials from two constituents has been demonstrated. The thickness of equally thick layers (i.e., equal volume fractions) is systematically varied. The yield strength of layered materials deposited by both schemes increases with decreasing layer thickness. When the layer thickness of the lower modulus constituent is greater than a critical thickness, the data are consistent with an Orowan type mechanism, and the strength varies approximately inversely with the layer thickness. The existing theoretical relationships appear suitable for designing layer architectures in this layer spacing regime. However, when the layer thickness of the low modulus constituent is less than a critical thickness, the yield strength of the materials deposited by both schemes appears to be controlled by an interaction with the interface. Both the Koehler image force model and the Embury and Hirth mechanism result in similar agreement with the data for the Al/Cu system. The Koehler model predicts that the greater the shear modulus difference between two constituent layers, the smaller will be the critical layer thickness where interface interactions take over, and this is supported by the experiments conducted here. The yield strength of the materials is shown to level off when the layer thickness is thinner than the critical thickness.

SUMMARY

Model Al/Cu metal-metal multilayered nanolaminates have been successfully fabricated by the novel Jet Vapor Deposition™ process. The microstructure and mechanical properties of these JVD fabricated multilayered nanocomposites have been investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and nanoindentation methods. The structure of the Al/Cu multilayers was polycrystalline and had strong (111) texture. The yield strength was controlled by an Orowan type process when the layer spacings exceeded ~50 nm, whereas that of the nanocomposites with the layer thickness smaller than ~50 nm is controlled by interfacial interactions. This transition is consistent with predictions of the Koehler model, which indicates that the critical layer thickness of the low modulus constituent decreases as the difference in shear moduli between the two constituent layers increases. This study suggests that the JVD™ process could be used for making functionally graded nanolaminates with independently varying local modulus and strength.

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References