Nanoindentation study of electrodeposited Ag thin coating: an inverse calculation of anisotropic elastic-plastic properties

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Abstract

A new inverse method was proposed to calculate the anisotropic elastic-plastic properties (flow stress) of electrodeposited Ag thin coating utilizing nanoindentation tests, previously reported inverse method for isotropic materials and three-dimensional (3-D) finite element analyses (FEA). Indentation depth was ~4% of coating thickness (~10 μm) to avoid substrate effect and different indentation responses were observed in the longitudinal (L) and the transverse (T) directions. The estimated elastic-plastic properties were obtained in the newly developed inverse method by matching the predicted indentation responses in the L and T directions with experimental measurements considering indentation size effect (ISE). The results were validated with tensile flow curves measured from free-standing (FS) Ag film. The current method can be utilized to characterize the anisotropic elastic-plastic properties of coatings and to provide the constitutive properties for coating performance evaluations.

Key words: Nanoindentation, electrodeposited, Ag coating, anisotropic elastic-plastic property, FEA

Introduction

Metallic coatings are frequently utilized in different industry sectors to provide substrate protection or to realize various physical, chemical, or biomedical functions [1, 2]. Generally speaking, various fabrication techniques, including electroplating, thermal spraying, physical or chemical vapor depositions, exert different thermal-mechanical loading histories to the coating materials and lead to different microstructural anisotropy and texture of the coating layers [3, 4]. The resulted columnar or lamellar microstructures of the coating layers naturally give rise to the directionally dependent elastic-plastic properties, which may lead to different coating failure modes in the form of cracking, delamination, cavitation or buckling under service or abusive environment [2-10]. Therefore, quantitative relationship linking coating chemical compositions and processing parameters to their thermo-mechanical properties are desired in coating design and coating performance evaluation and optimization.

Various testing techniques have been introduced to quantify the elastic modulus, thermo- and electrical conductivity of various coatings in the open literature [11-14]. Small-scale testing and characterization methods, such as free-standing (FS) thin film tensile [15, 16], micro-cantilever deflection [17-19], nanoindentation [17, 20-23] and micro-pillar compression [24, 25], have been attempted to estimate the mechanical properties of coatings. However, due to the limitations of the testing methods and sample size, most of these techniques are only capable of measuring the coating properties in one direction and insufficient of characterizing the fully anisotropic elastic-plastic coating properties.

Among all the methods, nanoindentation is widely adopted to measure the mechanical properties for its conveniences in sample preparation and testing [20, 26-31]. With indenter contacting in-plane (parallel to coating) and out-of-plane (perpendicular to coating) surfaces, the coating hardness in both directions can be quantified. However, for the purpose of coating performance analyses, elastic-plastic properties in addition to hardness are required. Although many inverse algorithms have been developed to extract elastic-plastic properties for isotropic materials [32-35] from nanoindentation load-depth (P-h) curves, few methods have been proposed to estimate coating properties [11, 36, 37] because the large number of the anisotropic elastic-plastic parameters will render non-unique solutions.

For relatively thick coatings or bulk materials [11, 36], different inverse methods have been proposed to estimate the elastic-plastic properties with multi-indentations. For example, Nakamura and Gu [11] proposed a simplified transversely isotropic elastic-plastic model for the atmospheric-plasma sprayed NiAl coating with a thickness of $\sim 290\ \mu\text{m}$, and estimated the corresponding elastic-plastic parameters with dual-indenter: a Berkovich and a spherical indenter. In that study, the as-deposited surfaces of thick coatings were polished and multi-indenter method was used with a $20\ \mu\text{m}$ indentation depth to avoid the indentation size effect (ISE).

For relatively thin coatings, however, ISE will significantly influence the indentation load-depth response [30]. This is because the maximum indentation depth should be controlled to be less than 10% of coating thickness to avoid any potential effect from the substrate [17, 31, 38]. For example, for a coating with a thickness of $10\ \mu\text{m}$, the maximum indentation depth should be below $1\ \mu\text{m}$, where significant ISE can be anticipated.

Moreover, some thin antimicrobial coatings prepared with Ag and other nanoparticles [39-41] are much softer than thermal barrier coatings prepared from ceramic or intermetallic. It is extremely difficult to perform standard mechanical polishing operation on the as-deposited surfaces is. Therefore, the roughness of the as-deposited surfaces prevents the application of spherical indenters with larger indentation area [32, 39, 42].

In the current study, single indenter-based nanoindentation study was conducted on a thin Ag coating ($\sim 10\ \mu\text{m}$ thickness) prepared by electroplating method [39]. A new inverse method was developed to estimate the elastic-plastic properties of the anisotropic Ag coating with the consideration of ISE. Since Berkovich indenter is the most commonly used indenter among different nanoindentation testing platforms, the current method utilizes indentation responses from a single Berkovich indenter. The P-h curves were collected from two directions of the coatings rather than multi-indenter in one direction [11]. The elastic-plastic parameters of the coating were estimated by finite element parameter to match the predicted indentation responses with those from experiments. The inversely estimated flow stress curves for the L and T directions were compared with that measured by FS Ag film reported in the literature as methodology validation [16]. Finally, the applicability of the current method is discussed with future directions suggested.

Experiments

Polycrystalline nanostructure Ag coatings were electrodeposited onto a nickel (Ni) coated brass substrate ($20\times 20\times 0.6\ \text{mm}^3$). The thickness of Ag coating and Ni coating was $\sim 10\ \mu\text{m}$ and $\sim 7\ \mu\text{m}$, respectively, as shown in Figure 1 (b) and (d). The detailed description of the deposition process can be referred in [39].

The nanoindentation tests were conducted using a Hysitron TI950 Triboindenter along L and T directions with a diamond Berkovich tip as shown in Figure 1. Considering the substrate effect and coating thickness, the maximum indentation loading was 5 mN such that the maximum indentation depth (h_{Lmax} or h_{Tmax}) was less than 400 nm in both directions. The current indentation depth avoids the possible delamination which may occur during unloading [43]. Also, the maximum load was held for 10s to avoid creep behaviors in both indentation directions. Multiple indents were attempted and at least five P-h curves in each direction were obtained. The surfaces perpendicular to the T directions were polished using a standard method so the influence of surface roughness can be ignored. The typical P-h curves are shown as the solid red curve in Figure 2 where the upper bound (the maximum P-h curves) and lower bound (the minimum P-h curves) of each direction are shown. The different indentation responses could be attributed to the microstructural orthotropy of the polycrystalline coating. In the current study, the distance of each indents were kept as $\sim 2 \mu\text{m}$ to reduce the residual stress field induced by the surrounding indents [44]. Meanwhile, the indents near the Ag/Ni interface, highlighted in the white dotted box of Figure 1(e), are not considered since the interaction with the Ni substrate increased the measured elastic modulus and hardness of the indents in the T direction, which was reported in previous studies [45, 46].

Due to the very thin nature of the Ag coating, the surface perpendicular to the L direction, i.e., the as-deposited surface, cannot be polished to minimize surface roughness. In order to minimize the influence of surface roughness, the indents were observed under the Scanning Probe Microscopy (SPM). As shown in Figure 1 (c), the color contour indicates that the height differences within the $30 \times 30 \mu\text{m}^2$ observation region could be as high as

400 nm, hence the P-h curves in the L direction are influenced by the surface roughness if indents were located on uneven surfaces [47]. If significant differences were observed on the loading curvature in the L direction, the P-h curves were rejected. In addition, a series of low depth (~ 150 nm) indents in the L direction were conducted before deep depth indentation (~ 400 nm). The P-h curves were obtained with relatively small scatter as the dotted green curves in Figure 3, and these curves were utilized to guide the selection of the back curve (~ 400 nm) for the L direction. It should be noted that the challenges of surface roughness cannot be completely overcome at such small indentation depth. However, special care has been taken to choose P-h curves with minimized surface roughness influence, see the red curves shown in Figure 3, for the inverse calculations. Since the total indent area was greater than $1 \mu\text{m}^2$ and the grain size of the Ag coating is ~ 50 nm [39], each indent covers at least 5 grains. The current indentation responses can be considered as the overall response of the coating layer rather than from a single grain or a few grains. The averaged P-h curves from all the indents along a single direction (solid curves in Figure 3(a)) are used for the subsequent inverse analyses.

The simplified constitutive relationship

Different P-h curves are measured along the L and T directions as shown in Figure 3(a). The hardness values along the two directions are calculated as $H_T = 1.87$ GPa and $H_L = 1.42$ GPa using the well-known Oliver-Pharr method [48]. It should be noted that imperfect indenter and pile-up during indentation would affect the applicability of the Oliver-Pharr method [49]. So the contact areas were calibrated carefully before indenting on different materials to minimize these effects. The different hardness values along the two directions clearly indicate the existence of anisotropy in the current coating since

hardness values are dominant by the plastic properties [50]. In addition, no hardness gradient is measured through the coating thickness among the various indents in the T direction shown in Figure 1(e), which indicate that the hardness values of the Ag coating near the free surface are close to those near the Ag-Ni interface.

With these observations, the thin Ag coating was assumed as a transversely isotropic material for which the mechanical property is isotropic in the plane parallel to the coating surface. To describe the elastic-plastic behaviors of a transversely isotropic material, simplified constitutive equations based on Hill's criterions for yielding was adopted and the details were described in previous studies [11, 36]. Here, we briefly review the constitutive relations.

(1) Elastic constants

The elastic properties of transversely isotropic materials are described with five independent parameters as the following equations if the Y direction was assumed as the L direction and X - Z plane was the T - T plane:

$$\begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \gamma_{yz} \\ \gamma_{zx} \\ \gamma_{xy} \end{bmatrix} = \begin{bmatrix} 1/E_T & -v_{LT}/E_L & -v_T/E_T & & & \\ -v_{TL}/E_L & 1/E_L & -v_{TL}/E_T & & & \\ -v_T/E_T & -v_{LT}/E_T & 1/E_T & & & \\ & & & 1/G_T & & \\ & & & & 1/G_L & \\ & & & & & 1/G_T \end{bmatrix} \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{bmatrix} \quad (1)$$

where the relationship between Poisson's ratio v_{TL} and v_{LT} are shown as following:

$$\frac{E_L}{E_T} = \frac{v_{LT}}{v_{TL}} \quad (2)$$

And the in-plane (X - Z plane) shear modulus G_T can be expressed as:

$$G_T = \frac{E_T}{2(1 + \nu_T)} \quad (3)$$

In Equation (1), five independent elastic constants (E_L , E_T , ν_L , ν_{TL} and G_L) can then fully describe the elastic properties of a transversely isotropic material. The five independent constants are further simplified [11]: the Poisson's ratio ν_T is approximated as 0.3 for metallic materials [36], and the average of the two out-of-plane Poisson's ratio is taken to be equal to the in-plane Poisson's ratio:

$$\nu_T = 0.3 \text{ and } \nu_{LT} + \nu_{TL} = 2 \nu_T \quad (4)$$

The out-of-plane shear modulus G_L is also approximated similarly according to the definition of the in-plane shear modulus G_T as:

$$G_L = \frac{E_T + E_L}{4 * \left(1 + \left(\frac{\nu_{LT} + \nu_{TL}}{2} \right) \right)} \quad (5)$$

With the deduction and assumptions in Equation (4) and (5), the constitutive relationship of the transversely isotropic materials can now be fully described by the two independent elastic constants: E_T and E_L .

(2) Plastic constants

The plastic properties of a transversely isotropic material are defined with Hill's criterion for orthotropic materials. Hill's criterion for yielding [51] is modified for transversely isotropic materials as:

$$\begin{aligned} f(\sigma) &= \sqrt{\left(P(\sigma_{xx} - \sigma_{yy})^2 + P(\sigma_{yy} - \sigma_{zz})^2 + Q(\sigma_{zz} - \sigma_{xx})^2 + 2R\tau_{xy}^2 + 2R\tau_{yz}^2 + 2S\tau_{zx}^2 \right)} - \sigma_0 \\ &= 0 \end{aligned} \quad (6)$$

where σ_o is defined as the reference strength, which is the average of the two yield strength along the two directions (σ_{Lo} and σ_{To}) as shown in Equation (7):

$$\sigma_o = \frac{\sigma_{Lo} + \sigma_{To}}{2} \quad (7)$$

And P, Q, R and S are dimensionless constants that can be calculated with σ_o , σ_{Lo} , σ_{To} , τ_{Lo} and τ_{To} as

$$P = \frac{1}{2} \left(\frac{\sigma_o}{\sigma_{Lo}} \right)^2; Q = \frac{1}{2} \left(2 \frac{\sigma_o^2}{\sigma_{To}^2} - \frac{\sigma_o^2}{\sigma_{Lo}^2} \right)^2; R = \frac{1}{2} \left(\frac{\sigma_o}{\tau_{Lo}} \right)^2; S = \frac{1}{2} \left(\frac{\sigma_o}{\tau_{To}} \right)^2 \quad (8)$$

Upon yielding, isotropic power law hardening was assumed to simplify the hardening behavior with a single hardening exponent, n , for both the L and the T directions. The post-yielding behavior for the L and the T directions can then be expressed as:

$$\sigma_L = \sigma_{Lo} \left(1 + \left(\frac{E_L \epsilon_L}{\sigma_{Lo}} \right)^n \right); \text{ for } \sigma_L > \sigma_{Lo} \quad (9)$$

$$\sigma_T = \sigma_{To} \left(1 + \left(\frac{E_T \epsilon_T}{\sigma_{To}} \right)^n \right); \text{ for } \sigma_T > \sigma_{To} \quad (10)$$

where ϵ_L and ϵ_T are the isotropic plastic strain in the L and T directions, respectively. Similar to the elastic properties, the plastic properties are also simplified with reasonable deductions. The shear yield strength are approximated in a similar way as the von Mises yield criterion for isotropic materials following:

$$\tau_{To} = \frac{\sigma_o}{\sqrt{3}} \text{ and } \tau_{Lo} = \frac{\sigma_o}{\sqrt{3}} \sqrt{\frac{\sigma_{Lo}}{\sigma_{To}}} \quad (11)$$

Thus, the independent plastic constants in the present study are reduced to σ_{Lo} , σ_{To} and n (or σ_o , σ_{Lo}/σ_{To} and n). With the above approximations and assumptions for materials with low degree of anisotropy, the five material parameters to fully describe the transversely isotropic behaviors are: E_L , E_T , σ_{Lo} , σ_{To} and n (or E_L , E_T , σ_o , σ_{Lo}/σ_{To} and

n). The purpose of the current inverse method is therefore to estimate the values of these parameters via the indentation P-h curves.

(3) Nominal properties

The concept of nominal properties, i.e., the properties inversely calculated using the P-h curves shown in Figure 3(a) based on the isotropic material model, has been introduced in previous inverse studies of transversely isotropic materials [11, 37] because they can simplify the inverse process. Note that, the nominal properties would be different from the actual transversely isotropic properties since they do not include any anisotropy. Similarly, nominal properties are introduced in the current study and they are indicated with an overhang bar for each variable, i.e., $\overline{E}_T$ and $\overline{E}_L$ for nominal elastic modulus, $\overline{\sigma}_{Lo}$ and $\overline{\sigma}_{To}$ for nominal yield strength, and $\overline{n}_L$ and $\overline{n}_T$ for nominal hardening exponent. Figure 3(b) summarizes the flow chart of the inverse method and detailed explanations are described below.

Inverse method

(a) Determination of elastic properties

With the Oliver-Pharr method [48], the nominal elastic modulus can be calculated as $\overline{E}_T=68.84$ GPa and $\overline{E}_L=72.53$ GPa for the two directions, respectively. The 2 θ results from X-ray diffraction (XRD) [39] indicated the two dominant peaks of the current coatings are Ag (200) and Ag (111), therefore the elastic modulus values obtained above appear reasonable since they are close to the measured 63 ± 3 GPa in previous studied [16] and lower than the calculated value of 83.8 GPa for the <111> orientation. Since the difference between $\overline{E}_L$ and $\overline{E}_T$ is only ~5% and elastic anisotropy has a very small effect

on plastic indentation response, it is reasonable to replace E_L and E_T with $\overline{E_L}$ and $\overline{E_T}$, for the current Ag coatings, respectively. With the assumed equations for Poisson's ratio and shear modulus, the elastic properties of the Ag coatings are fully determined.

The current results for electrodeposited Ag coating are different from previous inverse study on thermal sprayed NiAl coating from Nakamura and Gu [11]: the NiAl coating had high anisotropic lamellar microstructure where the actual E_L is smaller than E_T , however, electrodeposited coating includes more small columnar grains [52] within the microstructure which leads to the observation that E_L is higher than E_T .

(b) Determination of plastic properties

1. Nominal properties for L and T directions

A newly developed inverse method [30] for isotropic materials is used to determine the nominal yield strength and nominal strain hardening exponent. The ISE is considered since the characteristic length (h^*) of Ag estimated through the Nix-Gao model [38] has been reported as 450 nm from previous studies [53, 54], and the current indentation depths were less than 400 nm. Generally, the origin of ISE was considered as the dislocation density within materials beneath the indenter [38], so 450 nm was assumed to be h^* for indentation responses in either direction. With the new developed method from Cheng et al. [30], the maximum indentation load without ISE, P_{Tmax}^S and P_{Lmax}^S , are corrected as 3.27 mN and 3.35 mN, respectively. Then, $\overline{\sigma_{Lo}}$ and $\overline{\sigma_{To}}$ were calculated to be 148.5 MPa and 275.9 MPa, respectively; and $\overline{n_L}$ and $\overline{n_T}$ were calculated to be 0.14 and 0.25, respectively.

Hereafter, σ_o and γ will be used instead of σ_{To} and σ_{Lo} as the un-determined parameters since the sum of the actual yield strength in the two directions ($\sigma_{Lo} + \sigma_{To}$) can be approximated by the sum of the nominal yield strength ($\overline{\sigma_{Lo}} + \overline{\sigma_{To}}$), and this assumption did not lead to significant difference on the final flow stress in the previous study of NiAl coating [11]. Following this, σ_o is calculated as 212 MPa, and γ remains to be determined to illustrate the anisotropy in the plastic behavior.

2. Determination of γ and n with Finite Element Analyses (FEA)

The only remaining undetermined elastic-plastic parameters are γ and n . To calculate the closest solution, a parametric FEA-based indentation study was carried out to calculate the maximum indentation loads in the two directions in order to compare with the experimental measurements as target values. Note that, the target load values should be P_{Tmax}^S or P_{Lmax}^S rather than 5 mN since ISE affects the indentation responses [30].

A 3-D FEA model, as shown in Figure 3(c), has been developed within the commercial FE package ABAQUS to simulate the indentation process of the Ag coating. The substrate was not included since the indentation depth was ~4% of the coating thickness. Two types of solid elements, i.e., C3D8 (8-node linear brick) and C3D4 (4-node linear tetrahedron), are employed, and a typical model has about 176990 elements and 74128 nodes. The model is constructed with fine mesh surrounding the indented region to ensure numerical accuracy, and it is also large enough (i.e., 20 times the contact area) to minimize the end-effects. The Berkovich indenter is modeled as fully elastic and the friction coefficient between the indenter and coating was assumed as 0.1 [55].

Figure 4(a) shows the FEA predicted maximum indentation loads in the T direction (y-axis) vs. those in the L direction (x-axis) for each parameter set of γ and n together with the experimentally measured data point shown as the black square. Since γ is the ratio of the yield strength in the two directions, its initial range is selected around the ratio of H_L/H_T (0.76) with four values: 0.5, 0.6, 0.7 and 0.8. The initial n is guessed as the average of the nominal hardening exponent ($\overline{n_{Ao}}$), which is 0.2.

Then, the 3-D FEA model in Figure 3(c) was utilized again to estimate the plastic properties. For each simulation case, the indenter penetrates the coating materials with the assumed parameter set of γ and n to the same depth as h_{Lmax} , and the corresponding P_{Lmax}^{FEA} in the L direction is calculated. Next, the input materials properties are rotated by 90° around the T direction, and the indenter penetrates the material to h_{Tmax} , and the corresponding P_{Tmax}^{FEA} is calculated in the T direction. Four sets of predicted P_{Lmax}^{FEA} vs. P_{Tmax}^{FEA} values can now be obtained for $n=0.2$, as shown by the four green dots in Figure 4(a).

With the initial guess $n = \overline{n_{Ao}} = 0.2$, the green dots in Figure 4(a) for the four γ values of 0.5, 0.6, 0.7 and 0.8, are all higher than the target measurement indentation load values shown as the black dot in Figure 4(a). Since higher n values enhance the indentation stiffness [50], the actual n value should be lower than 0.2. The probable n values subsequently tried are $n=0.14$, 0.16 and 0.18 for the parameter sweep. Finally, the family of simulated P_{Tmax}^{FEA} vs. P_{Lmax}^{FEA} dots is plotted in Figure 4(a), with different colors representing different n values. The most probable combination of γ and n can be chosen as the point closest to the target experimentally measured data point.

Results and discussions

In Figure 4(a), the blue triangle from $\gamma = 0.6$ and $n = 0.16$ is the closest point to the experimental results among all the 16 points, and the difference between target values and the calculated results on P_{max} is $\sim 3\%$. Thus, the estimated properties of the Ag coating were: $E_L = 72.5$ GPa, $E_T = 68.8$ GPa, $\sigma_o = 211$ MPa, $\gamma = 0.6$ and $n = 0.16$. Since the non-uniformity of the coating could be introduced by the electrodeposition process, local property variations can be expected as the range of P-h curves shown in Figure 2. The prediction of the properties was based on the average of the entire thin coating.

From the obtained data, it is observed that γ and n influence the indentation load responses in a monotonic manner as shown in Figure 4(a): higher γ values will increase the differences between P_{Tmax}^{FEA} and P_{Lmax}^{FEA} as indicated by the red arrow, and higher n values increase both the P_{Tmax}^{FEA} and P_{Lmax}^{FEA} following the trend of the black arrow. The two arrows denote two nonparallel directions separately, hence the result closest to the target point can be found with a certain set of γ and n values. Should more accurate elastic-plastic parameters be desired, further iterations of the parametric study following a similar approach can be carried out around $\gamma = 0.6$ and $n = 0.16$ to refine the γ and n values. However, too many finely resolved 3-D indentation simulations are time-consuming. Hence, an estimated solution set with an acceptable error range can be obtained using the current method.

Note that, conceptually, one can obtain the set of γ and n values as long as sufficient number of FEA indentation studies can be carried out. However, since the physically admissible ranges of n and γ are rather large, the brute force approach would not be

computationally feasible if the parameters are to be chosen randomly. In this study, the values of H_L/H_T and $\overline{n_{Ao}}$ were used to guide the initial selection of the ranges for γ and n , respectively, such that highly accurate results can be obtained with a small number of FEA-based indentation simulations. It will be most desirable to compare the current results with the ones obtained with the methodology proposed by Nakamura and Gu [11]. However, the original Nakamura and Gu [11] method relies on two indenters (one Berkovich and one spherical indenter) indenting in the same direction, and it did not take ISE into consideration. The current method uses a single Berkovich indenter indenting in the two orthogonal directions to quantify the coating anisotropy. Since no significant elastic modulus anisotropy is obtained for the coating in this study, an isotropic elastic formulation could potentially be used instead of Equation (1) in the inverse method [36, 56]. Indeed, the results indicate that the actual anisotropic indentation responses are more dominant by the plastic parameters rather than the elastic ones.

The nanometer-scale crystals within the current Ag coating yield higher flow stress than bulk Ag with grain size $\sim 40 \mu\text{m}$ [57] due to the well-known Hall–Petch effect. To validate the proposed inverse technique, Figure 4(b) compares the inversely calculated elastic-plastic behaviors in the L and the T directions with the stress-strain curve obtained from FS Ag film (thickness = $5.77 \mu\text{m}$) reported by Huang and Spaepen [16]. The FS Ag film was prepared with strong $\langle 111 \rangle$ textured structure using deposited method and the average grain size is below micrometer. The yield strength reported for the FS Ag film was $\sim 250 \text{ MPa}$, and it is quite close to $\sigma_{To} = 264 \text{ MPa}$ obtained in the current study. Also the stress values are matching each other when strain is $\sim 1.4\%$. Regarding the potential wrinkling of the FS film would render inaccurate strain

measurements at the initial stage of tensile test, this stress-strain curve from FS thin film before yielding could be ignored [16]. Considering these, the flow stress level measured from the FS thin film is similar to the stress-strain behavior in the T direction, and this comparison serves as validation of our inverse results. Furthermore, the tensile flow stress from FS Ag film was extrapolated as the solid blue curves shown in Figure 4 (b) using the data points after yield with the Hollomon equation (solid curve):

$$\sigma = K \varepsilon_p^n \quad (12)$$

where $K=639$ MPa and $n=0.128$. In addition, a perfectly plastic flow behavior with the yield stress of 360MPa is shown as the dotted curve. These two curves were used in the 3-D indentation simulations and the corresponding P-h curves (blue) are shown in Figure 5 to compare with the flow behaviors for the two directions obtained in this study. The similar P-h curves from FS Ag thin film and the current simulated P-h curves on T direction further validated our prediction.

For the thin coating (~ 10 μm) considered in this study, maximum indentation depth used is 400nm to avoid substrate effect. Meanwhile, it is possible to utilized recursive FE simulations come up with the actual yield strength and hardening behavior of the actual indented material, and assess ISE as the inferred properties could be compared to those from thicker electrodeposited Ag. However, thick electrodeposited Ag coatings, such as 20 μm , is required to avoid the possible substrate effect for indentation. Thus, we removed the ISE initially and utilized parametric study to find the closest solution. Also, The ISE comes from the geometry necessary dislocations (GNDs) within metallic materials [38] and that is the reason that the current results from FEA does not match experimental results. If a dislocation density based constitutive model for crystal

plasticity FEA [58] was utilized, the GNDs will be included and simulated results can match the experiments. However, there will be more parameters to calibrate and the inverse study is extremely difficult to establish. Compared to microelectromechanical systems (MEMS)-based testing methods including FS thin film tensile and micropillar compression, nanoindentation is more convenient in sample preparation. In addition, it is capable of testing in both the L and the T directions for anisotropy characterization. Hence, instrumented nanoindentation together with the proposed inverse method can be a convenient method to quantify the thin coating anisotropy, especially its elastic-plastic properties.

It has been shown that the plastic properties inferred through one instrumented indentation are non-unique, and the specific procedures described in this study will yield one set of properties [59-61], see Figure 4(a). Conceivably, there may also be other sets of completely different elastic-plastic properties that also produce similar P-h curves to the measured ones. In our previously work, a relationship between yield strength and nanoindentation hardness was adopted in obtaining a unique solution set for the individual phases in a multiphase steel, and reasonably good agreement has been obtained compared with those obtained from in-situ high energy X-ray test [32, 35]. As mentioned above, Berkovich indenter is the most commonly used among different nanoindentation testing platforms. More sophisticated indentation techniques involving two or more indenters will be valuable in validating and improving the current results, which can be the direction of future studies.

The main microstructural-level features describing a coating include: (1) grain size and grain morphology, (2) morphology of grain boundaries and intergranular defects/phases,

(3) intergranular defects, and (4) composition distribution across grains and grain boundary. These features determine the elastic-plastic properties of the coatings, especially the anisotropy [62]. The thick thermal sprayed NiAl coating [11] had a lamellar structure, so the stronger elastic-plastic response was found along the L direction. Different from that, the current thin electrodeposited Ag coating has stronger elastic-plastic response in the T direction than the L direction, and this anisotropic mechanical response indicates a possible columnar structure similar to those previously reported on electrodeposited Ni coatings [14]. However, these microstructural feature was not directly observable from the SEM images shown in Figure 1 given the nanometer-sized grains resulted from the electrodeposition process [39]. Generally, the micro/nanostructures of the electrodeposited coatings are characterized with XRD and transmission electron microscopy (TEM), and the inhomogeneous microstructures and surface morphologies have been reported in previous studies [13, 14, 39]. Thus, the current nanoindentation studies in the two directions not only demonstrate the existence of microstructural anisotropy, but also quantify the transversely isotropic elastic-plastic behaviors as a result of the nanocrystalline level characteristics [62]. Further nano- and micro-scale characterizations will be conducted to study the microstructures, e.g., textures [10, 44-46], within the current Ag coating.

In general, the microstructure features of an electrodeposited coating are controlled by the electrodeposited processing parameters, e.g. pulsed wave forms, current density, bath composition and constituents, temperature, additive type and concentration, and metal ion concentration. By adjusting the processing parameters, various coatings with a specific microstructure and textures can be fabricated. For example, when bismuth (Bi)

electrolyte is added to the bath solution in the current electrodeposition process, Ag-Bi coatings can be prepared: XRD patterns with higher intensity in the (111) direction were measured, and higher nanoindentation hardness in both directions were observed compared to the current Ag coating [39]. The inverse method developed in the current study can be further **validated choosing the bulk materials** and applied to the new Ag-Bi thin coatings to quantify the relationship among coating chemistry, processing parameters and the resulted elastic-plastic properties of the coating layers.

Conclusions

In summary, an inverse method was proposed to quantify the elastic-plastic properties of the anisotropic Ag thin coatings with nanoindentation tests, previously reported inverse method for isotropic materials, and FEA parametric study. Note that, the current method is suitable for transversely isotropic materials and coatings where the elastic anisotropy is not significant i.e., $E_{Lo}/E_{To} \approx 1$. For materials with strong elastic anisotropy, i.e., **single crystal metals**, Vlassak and Nix [63] observed indentation test tends to "even out" the elastic anisotropy, i.e., **the elastic moduli obtained via indentation were closer to each other than those determined by uniaxial tension or compression tests**. Other methods, e.g., resonance ultrasound spectroscopy [64], should be used in determining the elastic stiffness matrix.

The inverse results were compared with stress-strain curves from previously reported FS Ag thin film and the good agreement was found. Thus, nanoindentation study with the proposed inverse methodology is a practical and convenient method to quantify the elastic-plastic properties of the anisotropic coatings, especially the difference in plastic behaviors in the two directions. The inversely calculated properties illustrate the

relationship between the coating fabrication technique and its mechanical properties, and it enables coating designers to optimize the process parameters to achieve the mechanical properties of its intended use. In addition, the inversely calculated properties can be used as input material properties in coating performance simulations, i.e., scratch tests, peel tests, and deep indentation tests, to quantitatively study the adhesion strength between the coating and the substrate.

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Figures

Figure 1: (a) The sketch of Ag coating, (b) Scanning Electron Microscope (SEM) image of coating on as-deposited surfaces, (c) indents (highlighted in circles) in the *L* direction under SPM with contour color bars indicating surface height, (d) the SEM image of one coating sample on surfaces perpendicular to *T* direction, and (e) indents in *T* direction under SPM

Figure 2 The upper bound (solid) and lower bound (dash dotted) of the P-h curves obtained in the two directions and the small depth (~ 150 nm) P-h curves in the L direction

Figure 3: (a) P-h curves in two directions from experimental (solid) and corrected curves for FEA to match (dotted), (b) algorithms of inverse calculation, and (c) the sketch of the finite element simulation model with Berkovich indenter. (X denotes L or T)

Figure 4: (a) The calculated data points (P_{Lmax}^{FEA} & P_{Tmax}^{FEA}) with corrected experimental values, and and (b) the inversely calculated flow curves for the T and L directions compared with flow stress measured by FS film tensile test [16] with two possible curves for large strain (solid green curve extrapolated with Hollomon's equation and dotted green curve extrapolated with perfectly plastic assumption).

Figure 5 Comparison of P-h curves from indentation simulations with extrapolated Hollomon equation (solid curves) and perfectly plastic flow curve (dotted curve)

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