High strength-ductility of thin nanocrystalline palladium films with nanoscale twins: On-chip testing and grain aggregate model

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Received 20 September 2011; received in revised form 24 November 2011; accepted 26 November 2011

Abstract

The mechanical behaviour of thin nanocrystalline palladium films with an ~30 nm in plane grain size has been characterized on chip under uniaxial tension. The films exhibit a large strain hardening capacity and a significant increase in the strength with decreasing thickness. Transmission electron microscopy has revealed the presence of a moderate density of growth nanotwins interacting with dislocations. A semi-analytical grain aggregate model is proposed to investigate the impact of different contributions to the flow behaviour, involving the effect of twins, of grain size and of the presence of a thin surface layer. This model provides guidelines to optimizing the strength/ductility ratio of the films.

Keywords: Nanocrystalline film; Twinning; Tensile testing; Strengthening mechanism; Analytical modelling

1. Introduction

Thin palladium membranes constitute an enabling material in hydrogen storage [1], sensing [2], purification and separation technologies [3]. These membranes must be as thin as possible to ensure high hydrogen permeance while remaining mechanically stable [3]. The lack of ductility of thin Pd films [4], as observed for a majority of thin metallic films, is a key issue for these applications [5]. From a more fundamental perspective, the mechanical behavior of nanocrystalline Pd has received attention in recent literature dealing with several interesting scientific questions related to deformation mechanisms and the connection to the microstructure (see Grewer et al. [6], Ivanisenko et al. [7] and Rössner et al. [8] for experimental studies, and Bachurin and Gumbsch [9] and Stukowski et al. [10] for numerical modelling). The lack of ductility of thin metallic films is related to a poor strain hardening capacity due to the small grain size, similar to bulk nanocrystalline systems. The presence of nanotwins constitutes an attractive way to enhance the ductility of nanocrystalline metals without altering the high strength, as demonstrated for Cu [11–15]. Kulkarni and Asaro theoretically studied the deformation mechanisms in nanotwinned fcc metals like Pd, Cu, Al and Ag, addressing the problem from a more general perspective [16]. These authors found, for instance, a transition in the deformation mechanism which is a function of the twin lamella spacing, except for Pd. There are thus multiple motivations to investigate the behaviour of thin Pd films as a system combining both nano-grain sizes and nanotwins.
The Pd films studied in Idrissi et al. [17] exhibit high strength owing to the small grain size (~30 nm), a high strain hardening capacity and a moderate ductility of between 3% and 6%. The high strain hardening capacity of the films was understood to possibly result from dislocation/twin interactions based on detailed transmission electron microscopy (TEM) characterization of the individual deformation mechanisms and defect interactions, although other contributions were invoked, such as kinematic hardening. The freestanding films were deformed on chip by a microtensile testing technique [18–20]. In this paper the mechanical response of Pd films is analysed in detail and a semi-analytical model is developed in order to improve our understanding of the relationship between the heterogeneous nanostructure and the overall flow behaviour. The model is based on the collective response of an aggregate of grains with different twin densities. This model confirms the potentially large impact of the twins on the high strain hardening capacity, but also accounts for a long elasto-plastic transition and highlights the effect of a residual surface layer on one side of the test structures.

The outline of the paper is as follows. The experimental conditions and the on-chip tensile testing method are presented first. Then the stress–strain curves of the Pd films are analysed and the main TEM observations are summarized. The elementary grain aggregate model is described next, followed by a parameter identification, validation and parametric study.

2. Experimental study

2.1. Materials and methods

The principles of the on-chip tensile testing method used to measure the uniaxial stress–strain curve of thin freestanding films have been described in detail elsewhere [18–20]. The technique relies on relaxation of the internal stress present in one beam material to deform another beam attached to it. This technique allows a large number of tests to be performed on very thin films without the difficulties related to the manipulation of samples and to the measurement of extremely small loads, and without the need for external actuation. In order to fabricate the Pd test structures investigated in the present study the method involves the deposition of four different materials on top of a silicon wafer (see Fig. 1a).

1. A silicon dioxide (SiO$_2$) layer is deposited by plasma enhanced chemical vapour deposition (PECVD). This layer is 1 μm thick and acts as a sacrificial layer.
2. A silicon nitride (Si$_3$N$_4$) layer is deposited at 800 °C by low pressure chemical vapour deposition (LPCVD). This layer involves a high level of internal tensile stress (~1 GPa). The large internal stress arises from the thermal expansion coefficient mismatch between the silicon substrate and the silicon nitride layer.
3. A 5 nm thick Cr layer is deposited by e-beam evaporation. This layer ensures adhesion between the SiO$_2$/Si$_3$N$_4$ layers and the Pd layer to be deposited next.
4. Pure Pd films are deposited by e-beam evaporation with thicknesses of 80, 160 and 310 nm. The internal stress level in the Pd films is systematically measured using the Stoney curvature measurement technique.

The silicon nitride layer is patterned by classical photolithography followed by plasma dry etching with SF$_6$. The Pd films are patterned by lift-off photolithography to produce a dog bone shaped beam. Lift-off photolithography is a method to pattern thin films. In contrast to classical photolithography the photoresist is first deposited on the substrate and patterned. The target material is then deposited over the resist. The target material lying on the photoresist is lifted off by dissolving the resist with a solvent, e.g. acetone, while the material deposited between the resist pattern remains on the substrate [21]. Concentrated hydrofluoric acid (HF) (73%) is used to etch away the sacrificial SiO$_2$ layer in order to release the test structures from the Si substrate. Cr being resistant to HF, this layer remains present after the release step. Once the sacrificial layer is etched away the Pd beams are deformed under uniaxial stress until load equilibrium is attained between the specimen and the Si$_3$N$_4$ beam. The Si$_3$N$_4$ beam used to impose a displacement on the sample is called the actuator.

Fig. 1 presents a schematic view of a typical test structure before (Fig. 1a) and after (Fig. 1b) the release step. Several samples of varying lengths are needed to generate a full stress–strain curve (Fig. 1c). A simple mechanical analysis allows the extraction of the stress and the strain level in each test specimen, based on measurement of the displacement imposed on the test specimen [20] and of the elastic strain (also called the mismatch strain) in the actuator material using dedicated structures [22–24]. The displacement $u$ imposed on the test specimen is measured by scanning electron microscopy (SEM) as the distance between moving and fixed cursors (Fig. 1b). SEM is also used to measure the specimen and actuator dimensions after release. The total strain in the specimen is the sum of the mechanical strain $\varepsilon_{\text{mech}}$ and of the mismatch strain $\varepsilon_{\text{mis}}$ (which is equal to minus the elastic strain stored in the test specimen upon deposition):

$$\varepsilon_{\text{total}} = \varepsilon_{\text{mech}} + \varepsilon_{\text{mis}} = \ln \left( \frac{L_0 + u}{L_0} \right),$$

where $L_0$ is the initial length of the test beam. The stress is obtained by imposing force equilibrium between the actuator and the test specimen as:

$$F = \sigma_d S_d = \sigma S,$$

where $\sigma_d$ and $S_d$ are the stress and the cross-sectional area of the actuator beam, respectively, and $\sigma$ and $S$ are the stress and the cross-sectional area of the specimen, respectively. As the actuator material (Si$_3$N$_4$ here) deforms elastically, the stress in the sample is:
\[ \sigma = \frac{E_a}{L_0a} \left( \ln \left( \frac{L_{0a} - u}{L_{0a}} \right) - \varepsilon_{\text{mis}} \right) \frac{S_a}{S}, \]

where \( E_a \) is the Young’s modulus of the actuator, \( L_{0a} \) is the actuator length and \( \varepsilon_{\text{mis}} \) is the mismatch strain of the actuator. More details concerning the error analysis can be found in Gravier et al. [20].

TEM characterization has been performed using a Philips CM20 microscope (LaB\(_6\), 200 kV), while a TECNAI G2 (FEG, 200 kV) was used for high resolution TEM (HRTEM). A focused ion beam (FIB) was used to prepare and thin down TEM samples (see the supporting information in Idrissi et al. [17] for more details about FIB sample preparation).

2.2. Results and discussion

Fig. 2 shows the stress–strain curves for the three film thicknesses. Structures with different actuator versus specimen width ratios were measured in order to evaluate the reproducibility of the method and to account for material variations over the wafer. The repeatability is acceptable and is improved when the film thickness increases.

The yield stress defined at 0.2% offset strain (\( \sigma_0 \)) is equal to 450 ± 39, 690 ± 86 and 1030 ± 149 MPa for the 310, 160 and 80 nm thick films, respectively. The error is calculated by analysing the error propagation in Eq. (3) [25]. Another criterion based on the tangent modulus [26] was also used, giving essentially the same values (see Table 1). Table 1 collects together all the numerical values related to the results plotted in Fig. 2. An increase in yield strength with decreasing thickness has often been reported in the literature and related to a Hall–Petch type effect associated with the constraints on plastic flow induced by grain boundaries [4,27] (the grain size often decreases with decreasing film thickness) or from the presence of surface layers putting an additional constraint on dislocations [28,29]. Here the in-plane grain size does not significantly vary among the different film thicknesses (see further in Table 2). Furthermore, no oxide is present on the Pd surface, as confirmed by high resolution electron energy loss spectroscopy (HREELS) measurements (results not shown), in agreement with other literature reports for standard atmospheric conditions [30]. However, as explained above, the thin Cr adhesion layer is still present along one of the sides of

Fig. 2. Stress–strain curves. Raw data for the (a) 80, (b) 160 and (c) 310 nm thick films. The straight line corresponds to the elastic regime for the Pd samples with a slope equal to 120 GPa, as measured by nanoindentation. The notation \( TX \_Y \) used here means that the samples are tested in tension, with \( X \) representing the actuator width in microns and \( Y \) the sample width, also in microns.
the test specimen during the tensile test, playing a role similar to a passivation layer by confining one free surface of the Pd specimen. We will come back to this point in Section 3.1.

The internal stress $\sigma_{int}$ in the Pd films is measured by the wafer curvature technique [31], giving $\sigma_{int} = 420 \pm 20$, $730 \pm 40$ and $850 \pm 80$ MPa for the 310, 160 and 80 nm thick Pd films, respectively. These values correspond to the internal stresses of a Pd/Cr bilayer. Even though the Cr adhesion layer is only 5 nm thick it has a very high internal stress level which can significantly affect the overall measurement of internal stress. The impact of the Cr layer can induce an early localization or fracture of the Cr layer or to the stress minus the initial yield stress $\sigma - \sigma_0$, respectively. Note that, as can be deduced from the error analysis, the error in the extracted stress $\sigma$ increases with decreasing specimen thickness. The variation in $\sigma_{int}$ first increases with deformation and then progressively decreases. This graph reveals that the Considère criterion, predicting that necking starts when $\sigma - \sigma_0$ is not attained. Fracture occurs earlier. Imperfections such as roughness or grain boundary grooving and/or cracking of the Cr layer can induce an early localization or fracture of the Pd films [34]. In Fig. 3c the initial hardening rate $\Theta_0$ obtained by linearly interpolating the initial response down to $\sigma - \sigma_0 = 0$ is equal to about 60 GPa for the 310 and 160 nm thick films. The maximum expected hardening rate is about $E/50$ for a polycrystal with micron-sized grains [35]. This value would be equal to 2.4 GPa for Pd, i.e. more than one order of magnitude lower than the value measured in the present study (see Fig. 3c and Table 1). Such a high $\Theta_0$ signifies that regions of the material behave elastically while other parts are already deforming plastically, inducing a significant kinematic hardening contribution. A long elasto-plastic transition can thus constitute a first explanation for the high apparent strain hardening capacity of the films. Similar long elasto-plastic transitions have

Table 1
Summary of properties extracted for each film thickness by on-chip microtensile testing with different dimensions of the test structures.

<table>
<thead>
<tr>
<th>Property</th>
<th>Pd film</th>
<th>310 nm thick</th>
<th>160 nm thick</th>
<th>80 nm thick</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_0$ (MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2% Offset strain criterion</td>
<td>450 ± 39</td>
<td>690 ± 86</td>
<td>1030 ± 149</td>
<td></td>
</tr>
<tr>
<td>Tangent modulus approach</td>
<td>500 ± 43</td>
<td>690 ± 86</td>
<td>1100 ± 159</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{int}$ (MPa) (wafer curvature measurement)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In Pd/Cr bilayer</td>
<td>420 ± 20</td>
<td>730 ± 40</td>
<td>850 ± 80</td>
<td></td>
</tr>
<tr>
<td>Estimated in Pd layer</td>
<td>375 ± 20</td>
<td>655 ± 30</td>
<td>705 ± 70</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_0$ (%)</td>
<td>0.04 (T10_2), 0.012 (T10_1)</td>
<td>0.052 (T10_2), 0.044 (T15_2)</td>
<td>0.02 (T15_2), 0.018 (T15_1)</td>
<td></td>
</tr>
<tr>
<td>$\Theta_0$</td>
<td>~60 GPa</td>
<td>~60 GPa</td>
<td>~200 GPa</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The notation TX_Y represents a structure producing Pd in tension using a X µm wide actuator and a Y µm wide Pd specimen. Note here that tensile structures tend to break at the overlap between the actuator and the specimen before fracture of the Pd beams for T10_4, T10_4 and T10_1 of the 310, 160 and 80 nm thick films, respectively.

Table 2
Characteristic dimensions of the microstructure of the Pd films based on TEM observations.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Pd film</th>
<th>310 nm thick</th>
<th>160 nm thick</th>
<th>80 nm thick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm) (w and h)$^a$</td>
<td>26 ± 1 and 184 ± 8 nm</td>
<td>33 ± 2 and 100 ± 4 nm</td>
<td>35 ± 2 and 57 ± 2 nm</td>
<td></td>
</tr>
<tr>
<td>Twinned grains (%)</td>
<td>26</td>
<td>13</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Number of twins per twinned grain</td>
<td>1.4</td>
<td>1.5</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ w, grain width; h, grain height.
been observed in other nanocrystalline materials [26,36–38]. The $\Theta_0$ value for the 80 nm thick film is even larger, but it should be considered with caution due to the larger error associated with this specimen thickness. Note that in Haque and Saif [36] a similar increase in the hardening rate was observed when the thickness of the Al film was decreased to 100 nm.

Another possible origin of the high strain hardening capacity related to dislocation mechanisms has been addressed in Idrissi et al. [17] and in more detail in Wang et al. [39] by extensive TEM analysis. Fig. 4 shows the columnar grains and the grain size distribution of the three different Pd films before deformation. Statistical analysis of the grain size was performed on more than 200 grains across each cross-section. The distributions shown in Fig. 4 should be taken as qualitative due to stereological effects related to the cross-sectioning. The real distribution is narrower, as confirmed by preliminary plane views. A complex quantitative analysis of plane views is under investigation. All films contain nanotwins, but nanotwins are not observed in all grains. This means that twins are present before deformation, appearing during deposition of the films. Table 2 gathers together the microstructure information, i.e. grain size, average percentage twinned grains and number of twins per twinned grain. However, although samples were observed along different crystallographic orientations in order to capture as many twins as possible, it should be noted that, due to the random and non-textured orientation of the nanograins, these measured twin densities are still underestimates.

HRTEM was performed on two different specimens from the 310 nm thick Pd film: one undeformed (as-deposited) specimen and one specimen deformed up to 4% (see Fig. 5). Initially the twin boundaries are perfectly coherent (Fig. 5a). A loss of coherency of the twin boundaries takes place during plastic deformation (Fig. 5b). Twin boundaries act as barriers to dislocation motion as well as sources of dislocations. The dislocation/twin interaction mechanisms constitute a second possible factor, here an isotropic hardening contribution, explaining the large strain hardening capacity of the films. Note also that the fact that the grains have different twin densities constitutes a strong source of heterogeneity during initiation of the long elastoplastic transition. This source of heterogeneity will next be assumed to predominate over the heterogeneity arising from the differences in grain size, due to the relatively narrow grain size distribution.

3. Grain aggregate model

3.1. Presentation

A semi-analytical grain aggregate model has been developed to represent the plastic flow behaviour of the Pd films accounting for the potential impact of the Cr layer. This model is based on the idea that the grain behaviour depends on the number of twin boundaries inside the grains and on the mean grain size, as well as on the position of the grain with respect to the upper free surface or lower constrained (by the Cr layer) surface. The objective at this stage has been to limit the complexity and to focus on the physics through developing a simple one-dimensional (1-D) empirical model in the spirit of the so-called tangent modulus models [26]. In addition to the position of the grain, the only other source of heterogeneity is assumed to arise from the distribution of growth twins. Fig. 6 shows the schematic model used to describe the microstructure of the films. The presence of the Cr layer is taken into account as it influences the strength and the hardening of Pd films by adding a barrier to dislocation motion. This barrier prevents dislocations escaping [41]. The Cr layer can also crack, inducing a local stress concentration in the Pd film and relaxing the confinement on the dislocations. Note that more sophisticated numerical models have been applied to
nanotwinned Cu [11,40]. The model proposed in Jerusalem et al. [11] relies on crystal plasticity theory, probably not applicable here considering the very small grain size. The study presented in Yue et al. [40] is based on three-dimensional (3D) molecular dynamics simulations, requiring representative volume elements much smaller than the one of interest in this study.

More precisely, a Pd film is described as an aggregate of columns, each column being made up of $m$ grains (Fig. 6). There are $l$ different types of grains depending on the number $i$ of twins per grain, $i$ varying between 0 and $l - 1$. A twin (which means the two surrounding twin boundaries and the twin interior) is considered here as an entity separating the grain without taking into account the inner

Fig. 4. (a–c) Grain width distributions derived from the cross-section analysis (with no stereological correction) of the three film thicknesses. (e–g) Grain height distributions derived from the cross-section analysis of the three film thicknesses. (Inserts a–c) TEM dark field images of cross-sections of the 80, 160 and 310 nm thick Pd films, respectively. The grains have a columnar shape with a height of approximately half the film thickness. Average values are given with the standard errors.

Fig. 5. HRTEM images showing typical twin boundary structures in two different 310 nm thick Pd samples. (a) Coherent parallel twin boundaries observed before release. (b) Another nanoscale twin boundary strongly distorted after a strain of 0.04 has been applied to the sample.
The number of grains within the Pd sample thickness and the proportion of twins were chosen in accordance to the TEM observations. The position $p$ of a grain in a column accounts for the nature of the upper and lower interfaces of the grain (free surface, grain boundary or Cr layer). The vertical interfaces are grain boundaries (no effect of free lateral surfaces is taken into account, the specimen width being much larger than the grain size). Each type of column $k$ has a volume fraction $f_k$, $k$ varying between 1 and $P^m$. The information regarding the microstructure is known from experimental characterization (see above). The objective of the model is to calculate the evolution of the overall uniaxial stress $\sigma$ applied to the film as a function of the overall applied strain $\varepsilon$.

Each grain is modelled as a uniformly deforming entity characterized by an isotropic elastic–plastic behaviour. The Young’s modulus $E$ relates the stress to the elastic strain, $\varepsilon^{ed}$ as $\sigma = E\varepsilon^{ed}$; hence $\sigma = E(\varepsilon - \varepsilon^{pl})$. The hardening law giving the variation with the accumulated plastic strain $\varepsilon^{pl}$ of the flow stress $\sigma_i$ of a grain at a position $p$ and containing $i$ twins is described by:

$$
\sigma_{i, j}^p = \sigma_{00} + M_x\mu b K^p \left( \frac{1}{d_{eff}} + \frac{1}{\lambda_i} \right) \left( 1 + \beta_i \varepsilon^{pl} \right)^n, \quad (4)
$$

The first bracket in Eq. (4) represents the initial flow stress, involving the following parameters.

- The Peierls stress $\sigma_{00}$ which expresses the lattice resistance against dislocation motion.
- The stress needed to activate a dislocation source: $M_x\mu b K^p \left( \frac{1}{d_{eff}} \right)$, where $M$ is the Taylor factor, $x$ is a parameter, $\mu$ is the shear modulus, $b$ is the Burgers vector, $K^p$ is a constant depending on the confinement of the grain and, thus, on its position $p$, and $d_{eff}$ is the effective grain size. This term is directly based on Taylor’s theory [35,42]. The grains are so small that classical forest hardening plays a negligible role. Plastic deformation is carried by dislocations which nucleate at grain boundaries, cross the grain and sink in the opposite grain boundary or interface or escape from the free surface. The higher the grain boundary area, the larger is the probability of dislocations nucleating. The twin density $\rho$ does not influence this term. The non-dimensional $K^p$ parameter is influenced by the presence of the Cr adhesive layer, which adds a supplementary barrier to dislocation motion, reflected in an increase in $K^p$. The identification of $K^p$ will be explained later. The $1/d_{eff}$ dependence arises from the fact that the stress needed to activate a source is inversely proportional to the distance between the pinning points, which, in nanograins, is imposed by the grain size [38]. This distance is taken as the effective grain size, as in Cheng et al. [43]. The effective grain size is calculated by averaging the three dimensions of the grain, i.e.

$$
d_{eff} = \frac{H + 2R}{3}, \quad (5)
$$

where $H$ is the height of the grain and $R$ is the in-plane size. The grain size distribution can significantly affect the strain hardening of nanocrystalline materials by introducing an important source of kinematic hardening [44]. The present model does not explicitly take into account the grain size distribution, which is relatively narrow. However, a grain size distribution effect indirectly enters the model through the distribution of growth twins (see below). The inverse identification procedure will lead to scaling of the effects of both the isotropic and kinematic hardening through the adjustment parameters. At first order what primarily matters is to have both sources of hardening in the model.

- The influence of twins on the yield stress is taken into account through the term $\left( \frac{1}{\lambda_i} \right)$, where $\lambda_i$ is the twin spacing. As proposed in Chen et al. [45], the flow stress varies as a function of the inverse of the twin spacing, for the same reason as for the grain size. The twin spacing is taken here as the height of the grain divided by the number of twins.

The second bracket in Eq. (4) is the isotropic hardening part of the phenomenological Swift law, where $\beta_i$ is a parameter depending on the number of twins in the grain and $n_i$ is the strain hardening exponent. The parameter $n_i$ is taken to be constant and is very low for grains containing no twins ($i = 0$), as no source of strain hardening is available. The strain hardening capacity of grains involving twins ($i \neq 0$) is initially high because when plastic deformation proceeds twin boundaries become incoherent, with the presence of sessile and partial dislocations accumulating along the interface, and more impenetrable to dislocations (see, for example, Dao et al. [46] and Zhu et al. [47]). This increasing strength of the interface leads to a high strain hardening exponent. After a few percent deformation the interface reaches a fully incoherent state and its strength does not increase further. The source of strain hardening is then exhausted. This is treated mathematically by assuming that the exponent $n_i$ decreases with plastic deformation: $n_i = n_{init} - K d_i^{pl}$, where $n_{init}$ is the initial strain hardening...
exponent in twinned grains and $\kappa$ is a parameter to be identified.

The following strategy is used to estimate and homogenize the overall response of the film during deformation. The film is a two layer system composed of one Pd film on top of a Cr film undergoing the same strain. The response is computed incrementally by imposing a total strain increment $d\varepsilon$, with the objective of calculating the corresponding total stress increment $d\sigma$. The relationship between $d\varepsilon$ and the strain increment in the columns of Pd grains $d\varepsilon_k$ is:

$$d\varepsilon = \sum_{k=1}^{\rho} f_k d\varepsilon_k. \quad (6)$$

Then the iso-energy assumption is enforced in order to homogenize the behaviour among different columns. The iso-energy assumption has been shown to provide a realistic intermediate response in a 1-D problem compared with the iso-stress and iso-strain bounds [48]. Iso-energy means that

$$\sigma_1 d\varepsilon_1 = \sigma_2 d\varepsilon_2 = \cdots = \sigma_r d\varepsilon_r, \quad (7)$$

where $\sigma_r$ is the stress in column $k$. Based on Eqs. (6) and (7) the strain in a column $k$ can be expressed as:

$$d\varepsilon_k = \frac{d\varepsilon}{\sigma_k} \left(\frac{1}{\sigma_1} + \frac{1}{\sigma_2} + \cdots + \frac{1}{\sigma_r}\right). \quad (8)$$

Motivated by the aligned configuration of the grains in each column, iso-strain is assumed to average the response within each column, i.e. the strain increment in a grain of type $i$ located in a column of type $k$, $d\varepsilon_{ki}$, is equal to $d\varepsilon_k$.

The stress increment in a grain of type $i$ in a column of type $k$ is:

$$d\sigma_{ik} = E_{Pd} d\varepsilon_{ik}^{el} = E_{Pd}(d\varepsilon_k - \gamma_i d\varepsilon^{pl}), \quad (9)$$

where $d\varepsilon_{ik}^{el}$ and $d\varepsilon^{pl}$ are the elastic and plastic strain increments in a grain $i$ of column $k$, respectively, $\gamma_i$ is a constant equal to 0 if $\sigma_{ik} < \sigma_{y,ik}$ and equal to 1 otherwise, with $\sigma_{y,ik}$ being the current yield stress of a grain $i$ in column $k$. After some elementary algebra implying the use of the hardening law (Eq. (4)), the plastic strain increment in the Pd film can be written as:

$$d\varepsilon_{ik}^{pl} = \frac{d\sigma_{ik}}{A_i n_i \sigma_{y,i} \left(\frac{A_i}{A^l}\right)^{\frac{1}{n_i}}}, \quad (10)$$

where $A^l$ represents the first bracket of Eq. (4). Combining Eqs. (9) and (10) provides a solution for the stress and the plastic strain increment in a grain. The stress increment in a column $d\sigma_k$ is given by:

$$d\sigma_k = \sum_{i=0}^{l-1} f_{ik} d\sigma_{ik}, \quad (11)$$

and the total stress increment in the Pd film is given by:

$$d\sigma_{Pd} = \sum_{k=1}^{\rho} f_k d\sigma_k. \quad (12)$$

When adding the contribution of the Cr layer to the overall mechanical response Eq. (12) becomes:

$$d\sigma = w_{Pd} \sum_{k=1}^{\rho} f_k d\sigma_k + (1 - w_{Pd})d\sigma_{Cr}, \quad (13)$$

where $w_{Pd}$ is the proportion of Pd in the total thickness of the two layer system. The stress increment in the Cr layer is calculated as follows, under the hypothesis that Cr behaves elastically, the thickness being too small to allow any plastic deformation mechanisms [49], and that the Cr layer softens as a result of damage due to transverse cracking:

$$d\sigma_{Cr} = E_{Cr} d\varepsilon_{Cr}(1 - D) = E_{Cr} d\varepsilon(1 - D), \quad (14)$$

where $D$ represents the damage in the layer and $E_{Cr}$ is the Young’s modulus of Cr. $D$ is assumed to evolve linearly with $\varepsilon$ such as $D = \xi \varepsilon$ ($\xi$ is a parameter identified hereafter).

### 3.2. Parameter identification and validation

The parameters of the model have been identified in the following way. The microstructure parameters were determined from TEM observations. Two grains are considered over the thickness ($m = 2$) of each film as the average grain thickness is equal to 184 ± 8 nm for the 310 nm thick film, 100 ± 4 nm for the 160 nm thick film and 57 ± 2 nm for the 80 nm thick film. A preliminary parametric study has shown that the predictions are only weakly affected by the choice of $m$. The number of twins $i$ per grain depends on the film thickness: for the 310 and 160 nm thick films the grains contain 0, 1 or 2 twins, while the 80 nm thick film contains only 0 or 1 twin per grain. The volume fraction of each type of grain $f_{ki}$ is found from a statistical analysis of many TEM observations and is different for each film thickness (see Table 3 for the numerical values). The effective grain size is computed using Eq. (5) and the grain sizes measured by TEM, giving $d_{eff} = 78$ nm for the 310 nm thick film, $d_{eff} = 55$ nm for the 160 nm thick film and $d_{eff} = 42$ nm for the 80 nm thick film.

An approximate value of the Peierls stress for Pd is taken from the rule of thumb $\sigma_{00} \approx 2 \times 10^4 \mu$ giving $\sigma_{00} \approx 10$ MPa. The Taylor factor $M$ is taken to be 3, as generally considered for non-textured fcc materials, $\delta = 0.35$ (this parameter is generally between 0.2 and 0.5 [35], $E_{Pd} = 120$ GPa, $\mu = 3/8$ $E_{Pd}$ ≈ 45 GPa and $b = 0.27$ nm [21]. The value of $E_{Pd}$ was confirmed by nanoindentation tests [50]. The Young’s modulus of Cr, $E_{Cr}$, is equal to 275 GPa [51].

The strain hardening exponent $n_i$ is, as explained earlier, very small for grains without twins, i.e. $n_0 = 0.03$, while for twinned grains it is initially fixed at a high value of 0.5. The strain hardening exponent for twinned grains is supposed to decrease linearly with plastic deformation: $n_i = 0.5 - k\varepsilon^p$. This last parameter $k$ was chosen by minimizing the error between the experimental and numerical results (see further), with the constraint that $n$ becomes equal to $n_0$ at large strain. As two grains are present over the film thickness there are only two different $k^0$ because
there are only two different positions $p$, i.e. two different cases of confinement: the upper position where grains have one free surface and one grain boundary parallel to the surface, and the bottom position where grains have no free surface. The constant $K_{\text{bottom}}$ should thus be higher than $K_{\text{upper}}$ and the proportionality factor is equal to 1.1. This proportionality factor is such that $K_{\text{bottom}}$ is 10% higher than $K_{\text{upper}}$ due to the greater confinement, as shown by a recent study based on a strain gradient plasticity analysis [41].

Four parameters must be adjusted: $K_{\text{upper}}$, $\beta_i$, $\kappa$ and $\zeta$. These parameters are supposed to be independent of the film thickness. The 310 nm thick film response was used to identify these parameters. In order to reproduce the experimental yield stress of 450 MPa of this film $K_{\text{upper}}$ should be equal to 2.4. Note that the only tuning parameter affecting the yield stress is $K_{\text{upper}}$ due to the greater confinement, as shown by a recent study based on a strain gradient plasticity analysis [41].

The two main ingredients missing from the present model are the rate sensitivity, which probably plays a significant role if we are referring to twinned nanocrystalline Cu [52], and the grain size distribution, which influences the strength and spread of the elasto-plastic transition of materials with a magnitude that increases with decreasing grain size [44]. This last feature can also partly explain the poor agreement of the model with the experimental results for the 80 nm thick film. The argument given earlier that the inverse identification procedure will lead to proper scaling of the effects of both isotropic and kinematic hardening through the adjustment parameters is valid only if the distribution of grain sizes is similar for the different film thicknesses. The 80 nm thick film has the largest size distribution, but this must be confirmed by detailed quantitative plane view analysis. Furthermore, the value of the parameter $\eta_s$ not available in the literature and/or not measurable independently, has been fixed as realistically as possible.

Shishvan and Van der Giessen studied the size-dependent yield strength of freestanding Cu thin films using a discrete dislocation plasticity model with a focus on the importance of the distribution of the dislocation source lengths [53]. Their results on the impact of the grain size/film thickness ratio on the yield stress (plotted in Fig. 15 in Shishvan et al. [53]) are in quantitative agreement with the strengths measured in this study when using parameters adapted to Pd. It confirms the hypothesis that the early stage of plasticity is dictated by the size-dependent nucleation of dislocations, through the term $M\gamma_{\text{bd}}K^p\left(\frac{1}{\eta_s}\right)$ in Eq. (4).

The origin of the strength increase with reducing film thickness is here due both to differences in the effective grain size of the various thickness films, to the presence of twins, which adds a term in the first bracket of Eq. (4), and to the presence of the Cr layer. This layer is a barrier which prevents dislocations escaping through free surfaces and which

Table 3
Parameters used in the model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>310 nm thick</th>
<th>160 nm thick</th>
<th>80 nm thick</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of grains over the film thickness $m$</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Number of grain types $k$</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>$D_0$ (nm)</td>
<td>78</td>
<td>55</td>
<td>42</td>
</tr>
<tr>
<td>$\lambda_1$ (nm)</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$\lambda_2$ (nm)</td>
<td>92</td>
<td>50</td>
<td>28</td>
</tr>
<tr>
<td>$\lambda_3$ (nm)</td>
<td>61</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Weighting factor $w$</td>
<td>98.4% Pd, 1.6% Cr</td>
<td>97% Pd, 3% Cr</td>
<td>94% Pd, 6% Cr</td>
</tr>
<tr>
<td>$J_{f0}$</td>
<td>0.74</td>
<td>0.87</td>
<td>0.92</td>
</tr>
<tr>
<td>$J_{f1}$</td>
<td>0.13</td>
<td>0.065</td>
<td>0.08</td>
</tr>
<tr>
<td>$J_{f2}$</td>
<td>0.13</td>
<td>0.065</td>
<td></td>
</tr>
</tbody>
</table>

$E$ of Cr = 275 GPa.
is a known source of the thickness dependence of the yield stress \([41]\). HREELS analysis confirms that the Pd surface is not oxidized (results not shown). Another interesting observation which can be made using the model is the increasing spread of the elastic–plastic transition with decreasing film thickness: the entire film becomes plastic at strains of 0.01, 0.019 and 0.022 for the 310, 160 and 80 nm thick film, respectively. This means that the relative contribution of kinematic hardening on the global strain hardening increases with decreasing film thickness. The kinematic hardening contribution in this model arises from the different behaviour of the different grains as a result of the presence or not of twins or of the Cr layer, depending on the position. Twins introduce heterogeneity at two levels, by changing the isotropic hardening response of the twinned grains and by effectively introducing a decrease in grain size through the \(1/k\) term in Eq. (4). Note that the local back stress resulting from the piling up of dislocations at grains boundaries or at twin boundaries is not taken into account \([54]\).

Now, starting from the identified set of parameters, they will be varied one by one in order to determine their effect on the mechanical response and provide insights into possible improvements in the properties. Fig. 8 shows the impact of twins on the global response of the 310 nm thick Pd film. The quantity of twinned grains is such that there is the same number of grains containing one twin as grains containing two twins. The higher the twin density, the higher is the strength of the Pd. The curve for 25% twins corresponds to the experimental data. Assuming that the grain aggregate model is at least qualitatively correct, the potential strengthening effect of adding more twins is great, as already observed for Cu films \([12]\). Fig. 9 shows the impact of the Cr layer on the stress–strain curve for the 310 nm thick film. The thinner the film, the more it will be influenced by the Cr layer because the Cr layer has a constant thickness of 5 nm. The predicted effect of the Cr layer, which acts as a passivation layer, is in good agreement with the data reported by Xiang and Vlassak \([29]\) and Puri et al. \([55]\).

The ductility can be estimated using Considère’s criterion. Fig. 10 shows the evolution of the ultimate strain and ultimate tensile stress when changing the grain size.
within the realistic range 40–200 nm, and the twin density of the 310 nm thick Pd film. The qualitative trend of the graph is the same for the other two thicknesses. Fig. 10a shows the impact of the twin density (from 0% to 100% twins) for different effective grain sizes. When no twins are present the ultimate strain decreases as the grain size decreases and the ultimate tensile stress increases. When the grain size is sufficiently small ($d_{\text{eff}} < 60$ nm) adding twins has a positive impact on both the strength and the ductility up to a twin density of about 25–50%. If the twin density exceeds the optimum density the ultimate tensile stress keeps increasing, but at the expense of a moderate decrease in the ultimate tensile strain. When the effective grain size is larger than 80 nm adding twins induces an increase in strength similar to that due to grain size reduction. Fig. 10b shows the same results as Fig. 10a but in a different way in order to highlight the effect of grain size when keeping the twin density constant. When no twins are present strengthening of the material at the expense of ductility with reducing grain size is again observed. These results demonstrate the potential to harden Pd films without a loss of ductility if an increased volume fraction of twins can be generated with small grain sizes. One way to decrease the grain size $d_{\text{eff}}$ is to break the columnar shape by depositing the films step by step in order to favour a more equiaxed shape. Note that no effect of twin boundary spacing on a change in dislocation mechanism leading to optimum twin spacing is taken into account in this work [15,56]. Finally, it is important to realize that the ductility is here predicted without accounting for possible imperfections and/or the rate sensitivity [57], which could definitely affect the predictions, although probably not the trends. Elimination of the extrinsic Cr layer can suppress one important source of imperfection.

4. Conclusions

This study was primarily aimed at elucidating the origin of the high strain hardening in Pd films. Experimentally, the uniaxial stress–strain responses of three Pd films of different thicknesses (310, 160 and 80 nm) have been extracted using internal stress actuated on-chip microtensile testing. A semi-analytical grain aggregate model has been developed, identified and validated. The features explaining the high strain hardening observed in the Pd thin films areas follows.

1. The presence of growth twins. The resulting microstructure is heterogeneous with a mixture of softer grains without twins and harder grains containing twins, explaining the high initial strain hardening with a large kinematic hardening contribution.
2. The loss of coherency of the twin boundaries during deformation also contributes to the evolution of the strain hardening exponent, providing a source for high isotropic hardening which is exhausted after a few percent deformation;
3. The presence of a Cr layer applies a degree of confinement to the grains next to it, artificially hardens the Pd films and probably has a negative impact on the ductility.

At this stage none of the two main sources contributing to the high strain hardening capacity, i.e. kinematic hardening due to heterogeneous flow versus isotropic hardening due to dislocation–twin boundary interaction, can be discarded or considered as playing a negligible role. Even a small contribution of forest hardening, not addressed here, could affect the response. Besides an understanding of the origin of the high strain hardening capacity, the model is able to capture the thickness effect observed experimentally. Additional experiments, based on films deposited under different conditions and possible heat treatments, are envisioned in order to separate the grain size effect, the twin density effect and the confinement effect.

Acknowledgements

The support of the Communauté Française de Belgique and of the Université catholique de Louvain through an
References