Available online at www.sciencedirect.com
SciVerse ScienceDirect
Acta Materialia 61 (2013) 40–50
Acta MATERIALIA
www.elsevier.com/locate/actamat

Manifestation of external size reduction effects on the yield point of nanocrystalline rhodium using nanopillars approach

Omar Alshehri [a,b,*], Mustafa Yavuz [a], Ting Tsui [a]

[a] Waterloo Institute for Nanotechnology (WIN), University of Waterloo, Waterloo, Ontario, Canada
[b] Industrial Engineering Department, College of Engineering, King Saud University, PO Box 800, Riyadh 11421, Saudi Arabia

Received 11 June 2012; received in revised form 2 September 2012; accepted 4 September 2012
Available online 11 October 2012

Abstract

In this study, pure rhodium was fabricated and mechanically investigated at the nanoscale for the first time. The nanopillars approach was employed to study the effects of size on the yield point. Nanopillars with different diameters were fabricated using electroplating followed by uniaxial compression tests. Scanning electron microscopy (SEM) was used as a quality control technique by imaging the pillars before and after compression to ensure the absence of cracks, buckling, barrelling or any other problems. Transmission electron microscopy and SEM were used as microstructural characterization techniques. Due to substrate-induced effects, only the plastic region of the stress–strain curves were investigated, and it was revealed that the yield point increases with size reduction up to certain limit, then decreases with further reduction of the nanopillar size (diameter). The later weakening effect is consistent with the literature, which demonstrates the reversed size effect (the failure of the plasticity theory) in nanocrystalline metals, i.e. smaller is weaker. In this study, however, the effect of size reduction is not only weakening, but is strengthening-then-weakening, which the authors believe is the true behavior of nanocrystalline materials.

Keywords: Nanopillars; Nanocrystalline materials; Nanomechanics; Size effect; Rhodium

1. Introduction

Rhodium is a rare and expensive member of the platinum group metals [1]. It was discovered in 1803/1804 by the English chemist William Hyde Wollaston in a crude platinum ore [2]. In its bulk form, pure solid rhodium has a silvery white color [3], and a rosy color in solution. Rhodium has a face-centered cubic (fcc) crystal structure, with no allotropes [4], and has an atomic number of 45, with an electronic configuration of [Kr] $4d^8\ 5s^1$ that has 38 isotopes [5].

1.1. Mechanical properties of bulk rhodium

Rhodium is one of the least studied of all metals. This is due to two reasons: first, it is extremely difficult to work with [6,7], and is more difficult to work with than other metals of similar crystallographic structure, such as Cu, Ag, Au, Pt and Pd [4]. This is partly due to its high melting temperature (1960 °C), which makes it difficult to be heat treated, for example. The second reason is that rhodium is an expensive yet rare metal. This is why Maurer et al. [8] reported in 1997 that the "experimental data concerning the elastic behavior of pure single-crystalline rhodium are hard to find in the literature" (they only found one paper concerning it). However, their sentence still holds true today: to the best of our knowledge, only five papers have studied the mechanical properties of non-alloyed or pure rhodium [6–10], two of which [8,9] neither discussed the plastic properties nor used the conventional tension/compression method, but rather applied the ultrasonic attenuation approach. The other three papers used the uniaxial tension test (no compression test was reported). Therefore, it a challenge to report the nanomechanical properties of Rh and compare them to their bulk counterpart.

* Corresponding author.
E-mail address: oalshehri@ksu.edu.sa (Omar Alshehri).

1359-6454/$36.00
http://dx.doi.org/10.1016/j.actamat.2012.09.009

Among the aforementioned papers, Holden et al. [10] fabricated 2540 μm daimeter the closest fit to our needs. They fabricated rod-shaped Rh samples by two methods: (i) as-received annealed specimens (no information on how the as-received specimens were fabricated) and (ii) annealed electron-beam floating-zone melted specimens. Both methods produced polycrystalline Rh rods. Looking at all different values for different fabrication and testing conditions in the aforementioned study, it is clear that the most suitable and proper value of yield point to show the external size effect (by comparing it to nanopillar yield point) is the value of the as-received sample at 25 °C temperature (room temperature), which is 67 MPa. Further details of the process are in Ref. [10]. Note that the external size is any length that can be measured from outside the material (e.g. the pillar height) vs. the internal size, which is the size measured at the interior of the material, such as the grain size/grain length. In this study, the external size refers to the diameter, and the "external size effect" is abbreviated to "size effect".

The manifestation of the size effect on the yield point upon scaling from the bulk to the nanoscale is discussed in the following sections.

1.2. Different methods used to study the nanomechanical properties

There are many methods used to study the mechanical properties of materials. For the nanomechanical properties, the possibility of using all these methods is reduced because of either technical or monetary reasons. The methods that have been applied to study nanomechanics are as follows: nanoindentation [11], uniaxial tension [12], uniaxial compression [13], three/four-point pressing [14], the plane-strain bulge test [15] and the crack propagation test [16].

All the above methods should presumably lead to the same conclusion about a certain property. However, there are some properties that cannot be studied by all of the above methods. The factors that limit the number of tests that can be applied are as follows:

1. The property that is intended to be investigated. For example, the yield point cannot be determined by nanoindentation.
2. The physical properties of the material under testing. For example, graphene cannot be studied by nanoindentation as there is no thickness for graphene to be penetrated.
3. The chemical properties of the material under testing. For example, sticky materials cannot be studied by the plane-strain bulge test as they will stick to and contaminate the surface of the bulge.
4. Embedded inaccuracies. For example, nanoindentation introduces a nonuniform distribution of the mechanical strains within the contact area as a result of using sharp pyramid tips, which "locally concentrate stress at the apex of the contact and along the edges of the pyramid" [17].
5. The shape of the specimen. For example, spheres cannot be studied by the plane-strain bulge test.
6. The cost of the test. For example, uniaxial tensile test for nanopillars is very costly and technically difficult because it involves many nanofabrication techniques (just for the sample preparation), and the tests and their set-ups should be done in individual basis, which limits the number of tests can be done.

1.2.1. Uniaxial compression of nanopillars

In light of the above factors, the most common technique for exploring nanoscale mechanical properties with the fewest limitations and drawbacks – especially that of the presence of strong strain gradients – is uniaxial compressive loading of cylindrical nanopillars fabricated by focused ion beam milling, whether alone [13] or coupled with electroplating [18]. This approach was first introduced by Uchic et al. [13] for microsized pillars, and was later extended to the nanoscale by Greer et al. [19] and others.

In such a test, the compression is done using a nanoindentation device outfitted with a flat tip (there is no nanoindentation involved; the nanoindenter tip is larger than the pillar and is neither round nor pyramidal but is flat, and thus acts as a compression tip). The stress–strain curve is simultaneously drawn for the compressed pillar.

1.3. Rhodium nanopillars fabrication techniques

Having chosen the appropriate method to study the nanomechanics (uniaxial compression of nanopillars), there are eight methods that can be used to fabricate Rh deposits (thin films and/or nanopillars), the first five of which have already been used to fabricate Rh deposits, whereas the last two are potential techniques for doing so. The methods are as follows: magnetron sputtering [20,21], electrospinning [22], plasma-enhanced chemical vapor deposition [23], physical vapor deposition [24,25], thermal deposition [26], electrochemical deposition [27], nanoskiving [28] and capillary force lithography [29,30].

Of these techniques, electrochemical deposition, or electroplating, was chosen for several reasons. First, it provides high quality results at a low cost. Second, it is simple to implement relative to other techniques that require sophisticated machines and equipments. Third, electroplating provides uniform and less contaminated deposits as no gas is needed in the process – a property that is most important with the fine nanotemplates or holes that our chips possess, as will be described later. Fourth, electroplating makes it possible to fabricate sub-100 nm pillars [12,31], which is difficult using other methods. Moreover, electroplating offers a better chance of filling the very small templates.