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Elevated temperature, micro-compression transient plasticity tests on nanocrystalline Palladium-Gold: Probing activation parameters at the lower limit of crystallinity

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ABSTRACT

In this study, we probe the activation parameters and time-dependent plastic behavior of a nanocrystalline Palladium-Gold alloy by means of elevated temperature micropillar compression experiments. All tests were conducted on a stable, displacement-controlled *in situ* SEM indenter. A series of strain rate jump tests, where the strain rates were varied from 10^{-4} s^{-1} up to 10^{-2} s^{-1}, allowed us to extract strain rate sensitivity and average activation volumes in the order of 8 b^3. Repeated load relaxation tests yielded lower activation volumes in the range of 4 b^3. From the variation of test temperatures up to 125 °C, we extracted an apparent activation energy of ~0.77 eV. The possible deformation mechanisms at such extremely small crystallite sizes are discussed within the framework of pertinent literature.

1. Introduction

Compared to conventional polycrystalline *fcc*-metals, nanocrystalline metals provide excellent mechanical properties [1–3], which makes these materials very attractive for a variety of engineering applications: MEMS devices, microcomponents for medical applications or watch parts. The key parameter that determines the mechanical properties in these materials is their extremely fine grain size, which is the cause of both, their greatly improved strength and their time-dependent plastic behavior. However, although numerous studies have dealt with the determination of the rate limiting processes in nanocrystalline materials it has not been possible so far to clearly identify the dominant mechanisms.

Looking at the upper limiting case of grain size, which is represented by conventional polycrystalline metals, pronounced ductility prevails and is caused by two essential features: the presence and stress driven multiplication of mobile dislocations which act as flow defects and propagate strain and, secondly, their work hardening capability which is an effect of intraplane dislocation interactions and autonomous cell structure formation [4]. The lower limit of grain size, where crystallinity vanishes, is the metallic glass where dislocations as such are unstable and therefore not available as carriers of plastic flow. Due to the lack of any long-range order, straining of metallic glasses promotes the occurrence of localized shear transformation zones (STZ) [5] which propagate strain by shuffling and flipping of entire groups of atoms. At higher strains STZ's accumulate in regions of strain localization and form shear bands which may consequently propagate through the material and lead to failure [6]. However, the plasticity of nanocrystalline metals, which in terms of crystallite size resides in-between these two extreme cases, is much more complex to understand. As the grain size is reduced, the relative amount of volume occupied by grain boundaries increases reciprocally. For example, the grain boundaries occupy volume fractions as large as ~5–10% for grain sizes of 50 nm [7,8]. Smaller grains are less effective in generating dislocations, and hence their ability to

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interact across intercrystalline domains is reduced. Particularly, when grain sizes approach the limit of crystallinity towards the amorphous regime, grain boundary-mediated deformation processes gain influence while dislocation-mediated processes fade. Mechanisms which essentially emerge from the core regions of grain boundaries, such as grain boundary sliding [9–11], grain boundary migration [12–15], STZ activity in the grain boundary core region [5,16–18] and dislocation nucleation from grain boundaries [3,19] are under debate. Consequently, both thermally-activated and stress-driven deformation processes can be simultaneously operative in these materials [20,21]. All of these mechanisms contribute to the marked time-dependent plasticity of nanocrystalline metals, manifesting itself as a high degree of strain rate sensitivity and susceptibility to load relaxation and creep even at room temperature.

In this study, we explore the strain rate sensitivity and the load relaxation properties of a highly pure nanocrystalline $Pd_{90}Au_{10}$ alloy with a nominal grain size of $d_{Pd90Au10} \cong 12$ nm by means of dynamic micropillar compression experiments at elevated temperatures. First we briefly discuss the testing technique, our experimental considerations and data analysis methods. Then we focus on the applicability of this type of micromechanical experiment for probing activation parameters in nanocrystalline materials. Finally, the results of both types of tests are discussed and compared to literature data to gain insights into the possible rate controlling deformation mechanisms in these materials. To the best of our knowledge there is no micropillar transient test data for materials with such low crystallite sizes available in literature.

1.1. Considerations on time-dependent metal plasticity

For the proper understanding of the analysis and results presented in this work it seems helpful to recapitulate the concepts on which transient tests (i.e. load relaxation and strain rate jump tests) are based upon. In this section, we therefore give a brief overview of the basic concepts and discuss their applicability with reference to nanocrystalline metals.

The most general approach is to write $\dot{\gamma}$, the net shear strain rate for applied stresses, τ, close to the athermal threshold stress, in the form of an Arrhenius term:

$$\dot{\gamma} = \dot{\gamma}_0 \exp\left(-\frac{\Delta G\left(\tau, \widehat{\tau}\right)}{kT}\right). \tag{1}$$

The standard notation is used here where k is the Boltzmann constant and T is the absolute temperature. Here, ΔG is the Gibbs free energy of that is related to thermally overcoming the resistance originating from an energy barrier for a shear process that propagates strain along the activation path. The maximum level of deformation resistance is given by $\widehat{\tau}$, the athermal threshold stress. When $\widehat{\tau}$ is approached by τ, the activation free energy ΔG tends to zero, which describes the transition from thermally activated to athermal deformation [22]. The pre-exponential factor, $\dot{\gamma}_0$ represents a reference strain rate, which is usually regarded as a constant; a supposition that seems valid whenever a specific mechanism dominates strain propagation. The nature of a specific activated process can be characterized by the (shear) activation volume V_a, which is defined as $V_a := -\partial \Delta G / \partial \tau$ at constant pressure and temperature. Combining the definition of V_a and Equation (1), it can be inferred that

$$V_a = kT \left.\frac{\partial \ln \dot{\gamma}}{\partial \tau}\right|_{T,P}. \tag{2}$$

The activation volume as presented in Equation (2) has been formulated in a more general form that is applicable to all sorts of inelastic relaxations which are kinematically possible, regardless of the mechanism. Since it is a priori not known which mechanisms contribute in which manner to overall deformation, ΔG should be interpreted as an apparent free energy of activation and consequently V_a then also represents an apparent activation volume.

The magnitude of activation volume may help to identify and discriminate between different possible thermally-activated and rate-controlling deformation mechanisms. It can be extracted from any transient test: strain rate jump, creep or load-relaxation tests. Generally, the smaller the activation volume is the more localized the rate-controlling mechanism has to act in order to propagate plastic deformation. Large mechanisms like forest dislocation cutting have characteristic activation volumes on the order of 1000 b^3 ($\approx 2 \times 10^1$ nm^3), whereas small mechanisms like kink pair formation or point defect migration, being characteristic of creep processes, exhibit values in the range of 0.02–1 b^3 ($\approx 2 \times 10^{-3} - 4 \times 10^{-4}$ nm^3) [23]. Intermediate values of activation volumes associated with mechanisms like shear transformation plasticity (5 b^3) [24,25] and partial dislocation activity (10 b^3) [26] both represent deformation modes which are considered as plastic strain carrying mechanisms in nanocrystalline materials.

Subsequently, analysis routine for load-relaxation tests under constant-strain conditions will be described. For strain rate jump tests (SRJT), please see available references, i.e.: [27–31]. In a load-relaxation test (LRT), the externally applied deformation is stopped and the stress drop $\Delta\tau$ recorded over time, while the applied strain is held constant. This decay in shear stress, $\Delta\tau$, varies with time t according to [32] as:

$$\Delta\tau = -\frac{kT}{V_{a,r}} \ln\left(1 + \frac{t}{c}\right) \tag{3}$$

where $V_{a,r}$ is the apparent activation volume under stress relaxation conditions and c is a time constant. In general, the apparent activation volume is a complex activation volume reflecting the proportional shares of all deformation mechanisms acting at a specific stress/strain state in the material. It can be extracted from different evaluation protocols and is subjected to microstructural evolution during data collection. As a result, the apparent activation volume does not necessarily relate to a single deformation mechanism.

In the context of dislocation plasticity, the nominal effective activation volume, V_e, has been introduced and can be investigated using transient tests [32,33]. Hence, a repeated micropillar stress relaxation test (RLRT) has been recently developed [34] in order to probe V_e in thin films or in cases where bulk material is not readily available. In detail, constant strain relaxation is sequentially measured while in between each relaxation segment the sample has been reloaded (apparently elastically) to the initial stress condition. The effective activation volume can then be extracted from the reloading steps by means of Equation (4). V_e is then related to subsequent strain rate values at the end (f) and beginning (i) of relaxation segments and the associated stress difference $\tau_{i,j+1} - \tau_{fj} = \Delta\tau$, where j denotes the j-th relaxation segment in a given relaxation cycle (see Fig. 7):

$$V_e = kT \frac{\ln\left(\dot{\gamma}_{i2} \middle/ \dot{\gamma}_{f1}\right)}{\Delta\tau_{i2-f1}} = kT \frac{\ln\left(\dot{\tau}_{i2} \middle/ \dot{\tau}_{f1}\right)}{\Delta\tau_{i2-f1}} \tag{4}$$

The form of Equation (4) represents the difference quotient of Equation (2) and, therefore, manifests a stress-average or effective activation volume; in the second expression of Eq. (4), it has been