Can we use kinetic analysis for investigation of deformation processes in nanocrystalline materials?

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Abstract. Present paper represents an examination of strain rate response of nanocrystalline (NC) Pd with the aim to shed a light at deformation mechanisms operating in this material with extremely small grain size of 14 nm. Specimens were prepared by inert gas condensation method, and studied using conventional and in situ in SEM compression tests, and instrumented high pressure torsion (HPT). NC Pd demonstrated very high compression strength and good ductility, furthermore, strain rate jump tests revealed high strain rate sensitivity of 0.05, and corresponding activation volume was only 5\textsuperscript{b}. Microstructure investigation in the gauge sections revealed signatures of various deformation mechanisms: dislocation slip, twinning, cooperative grain boundary sliding and shear banding. These results raise a question about the applicability of kinetic analysis for nanocrystalline materials.

1. Introduction
The mechanical behaviour (strength, ductility, mechanisms of deformation, strain hardening) of nanocrystalline materials is not yet understood and is one of the key topics of modern material science. A major impediment to studies of the deformation of nanocrystalline metals is their typically very limited ductility in tension, which restricts the experimentally accessible parameter space. Compression tests and torsion testing under high pressure [1,2] offer an important opportunity, since they allow practically unlimited shear strain without fracture.

In this paper we study the deformation behaviour of NC Pd at low strains (using ex situ and in situ in SEM compression tests) and large strains (using instrumented high pressure torsion (HPT)). We also perform the analysis of plastic deformation kinetics in NC materials by means of strain rate change (jump) tests.

2. Experimental
Nanocrystalline Pd with a mean grain size of 14 nm (figure 1a) was obtained by inert gas condensation. Uniaxial compression tests were performed using a dedicated testing machine for miniature specimens with dimensions 0.9 mm×0.9 mm×1.3 mm. The strain was precisely measured by means of a laser extensometer P-50 from Fiedler Optoelectronics. The instrumented HPT tests were performed in a compression-torsion mode under a pressure of 4.5 GPa in a Schenck\textsuperscript{TM} testing machine using three strain rates (\textsuperscript{\textdegree}): 1 s\textsuperscript{-1}, 10\textsuperscript{-1} s\textsuperscript{-1} and 10\textsuperscript{-2} s\textsuperscript{-1}. All experiments were performed at room
temperature. For conventional bright and dark field imaging, a Phillips CM 30 operated at 300 kV was used.

3. Results

3.1. Deformation behaviour of NC Pd in compression tests

As-prepared igc Pd with a homogenous nanocrystalline microstructure demonstrated pronounced strain hardening, very high compression strength and good ductility (figure 2). The compression stress ($\sigma$) is significantly rate-dependent: strain rate sensitivity coefficient $m$, obtained from the jump tests, is estimated as:

$$m = \frac{\partial \log(\sigma)}{\partial \log(\dot{\varepsilon})}$$

yielding 0.05, and activation volume defined as:

$$\Delta V = \sqrt{3kT/m\sigma}$$

where $k$ is the Boltzmann constant and $T$ is the temperature, is equal to $5b^3$ ($b=$Burgers vector).

3.2. In situ observation of the development of deformation relief during compression test

Using the special technique of grey-scale correlation analysis, it was revealed that NC Pd specimens were deformed homogeneously only until the yield point, and after that the sample was sheared along planes inclined at around 45° to the compression axis. Further compression led to greater shearing and buckling in the middle of the gauge length. Careful inspection of the sample surface revealed great number of shear bands emerging and multiplying during loading. These shear bands are seen as very narrow but distinct lines distributed with a spacing of 10µm (figure 3).

3.3. Instrumented HPT test

The mechanical response and the microstructure development during HPT in a very wide range of strain and strain rate in NC Pd was studied in [2]. Typical Torque vs. shear strain curves for the strain range $\gamma<$15 are shown in figure 4. Very similar to the results of compression test, rapid strain hardening, high strength and strain rate sensitivity is observed. The microstructure investigation of the HPT processed samples revealed a larger grain size at the strain value $\gamma = 15$, where the mean grain size was $D = 40$ nm, more than twice the initial value. At an aspect ratio of 1.1, the grains appear still equiaxed at this strain. Dislocations and their pile-ups - spreading throughout entire grains – can be found in larger grains with diameter $>$50 nm. Importantly, however the fraction of grains with dislocations is rather low, most grains are visibly free of dislocations. Some amount of twins in the form of thin lamellae is also observed inside of many grains. Remarkably, a formation of planes of cooperative grain boundary sliding was observed very frequently. A typical example is shown in Fig. 1b.

Figure 1.

Microstructure of NC Pd in the as-prepared igc state (a) and after HPT for $\gamma =$15 showing formation of planes of cooperative grain boundary sliding. Reprinted from [2] with permission of Elsevier.
4. Discussion

We start our discussion with the analysis of strain rate sensitivity and activation volume revealed in compression test. The values of m and $\Delta V$ are consistent with those obtained for electrodeposited Ni with a grain size of 30 nm [3,4,5,6,7] and point to a thermally activated control of plastic deformation in NC Pd. On the other hand they are inconsistent with values typical for all known deformation processes: dislocation glide, creep, grain boundary sliding. This fact led many scientists to conclude that some special kinds of dislocation mediated mechanisms are operating in NC materials [6-8,9]. For example it was shown that dislocation nucleation on grain boundaries should be thermally activated [7,8]. Furthermore a propagation of a dislocation loop through the grain would require thermal assistance to overcome various obstacles such as dislocation tangles in a narrow area next to a grain boundary [10], pinning at grain boundary ledges [8], or at grain boundary impurities [7]. All these “obstacles” are localised to a very small spacing at/in the grain boundary with typical dimensions of 5-10 b$^3$, and calculation of corresponding m using Eq.2 would result in high m values close to those obtained experimentally.

Figure 2. Stress vs. strain compression curves of NC Pd with a mean grain size of 14 nm.

In this respect we would like to emphasise that our investigations revealed signatures of various deformation processes occurring in NC Pd with a grain size of 14 nm: from dislocation slip and twinning to cooperative grain boundary sliding (Fig. 1b) and shear banding (Fig. 3).

This raises the question about the applicability of kinetic analysis for NC materials. This analysis is valid for the case when the deformation mechanism uniquely determines the strain rate $\dot{\gamma}$. This strain rate is determined by the Arrhenian equation [11,12]:

$$\dot{\gamma} = \dot{\gamma}_0 \exp\left(-\frac{\Delta G(\tau_e)}{kT}\right).$$  \hspace{1cm} (3)

Here $\Delta G$ the Gibbs free energy of activation for the stress-assisted thermally activated process and $\tau_e$ the thermal component of the applied shear stress, i.e. the stress necessary to overcome the short range barrier responsible for the temperature and strain rate dependence. The pre-exponential factor $\dot{\gamma}_0$ depends on the volume fraction of fertile material that can take part in the configurational transformation, the characteristic frequency of the cluster or other configuration along the activation path (a cluster can be a dislocation line segment, or a twin embryo, etc.) and finally on a freestanding transformation shear strain [12], and represents therefore the rate of operating deformation process. Activation energy $\Delta G$ and activation volume $\Delta V$ can be found from following equations based on Eq.3:

$$\ln[\dot{\gamma}(T_1)/\dot{\gamma}(T_2)] = \frac{\Delta G}{k} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$  \hspace{1cm} (4)
when stress is constant, and

$$\ln\left[\dot{\gamma}(\tau_1) / \dot{\gamma}(\tau_2)\right] = \frac{\Delta V}{kT}(\tau_1 - \tau_2)$$  \hspace{1cm} (5)

when temperature is constant.

Obviously, these equations cannot be used in cases where more than one deformation mechanism controls the stress-strain relationship, because \(\dot{\gamma} = \dot{\gamma}_0 \exp\left(-\frac{\Delta G_1(\tau_1)}{kT}\right) + \dot{\gamma}_0 \exp\left(-\frac{\Delta G_2(\tau_2)}{kT}\right)\) is not an exponent, and taking its logarithm would yield an apparent activation energy \(\Delta G_1<\Delta G<\Delta G_2\) gradually changing in the measurement ranges of temperature and stress [13]. The same is valid for the activation volume.

**Figure 3.** Torque vs. Shear Strain curve of NC Pd deformed at different shear strain rates. Only portion of the diagram up to shear strain \(\gamma = 1\) is shown.

5. Conclusions
A variety of deformation mechanisms are operating in NC Pd with a grain size of 14 nm during plastic strain. In case of several dominating mechanisms the application of the kinetic analysis may be hindered and may lead to confusing results. Careful analysis of microstructure in the gage section after test or/and in situ observation should be performed to justify the conclusions yielding from the kinetic analysis.

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