Elevated temperature, strain rate jump microcompression of nanocrystalline nickel

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Nanocrystalline and ultrafine-grained materials show enhanced strain rate sensitivity (SRS) in comparison to their coarse grained counterparts. Majority of SRS measurements on nanocrystalline thin films reported in literature have focused on nanoindentation-based approaches. In this paper, micropillar strain rate jump tests were demonstrated on an electrodeposited nanocrystalline nickel film from 25 to 100 °C. SRS exponent, $m$, and activation volume, $V$, values were determined as a function of temperature. The measured values were found to be in good agreement with previously reported literature on bulk and nanoindentation measurements. Apparent activation energy for deformation was found to be about $100 \text{ kJ/mol}$, which is close to that for grain boundary diffusion in nickel. Grain boundary sliding was observed in the deformed pillars from scanning electron microscopy images.

Keywords: strain rate jump microcompression; strain rate sensitivity; nanocrystalline nickel

1. Introduction

Nanocrystalline and ultrafine-grained materials show enhanced strain rate sensitivity (SRS) in comparison to their coarse grained counterparts [1]. Conventionally, SRS of these materials has been measured on bulk specimens, either in compression or in tension. These bulk experiments can be divided into two broad categories: constant strain rate (CSR) measurement experiments and strain rate jump (SRJ) tests. In CSR measurement experiments, multiple samples are tested at different strain rates and the dependence of flow stress as a function of strain rate is calculated. In SRJ tests, the strain rate is varied (single or multiple jumps) during the test, on a single sample, and the flow stress dependence on strain rate is determined. The advantages of SRJ tests include determination of SRS exponent, $m$, from a single test and shorter test duration. Additionally, the microstructure of the specimen immediately before and after the SRJ can be considered to be constant enabling the study of the governing deformation mechanism(s).
With the emergence of electrodeposition and magnetron sputtering as promising methods for deposition of controlled microstructures of nanocrystalline and twinned materials [2–5], it has become necessary to adapt bulk mechanical tests to smaller samples. Jonnalagadda et al. [6] measured the strain rate dependence of flow stress of microtensile specimens of 0.85 and 1.76 μm thick free standing Au films over eight decades of strain rates at room temperature. Karanjgaokar et al. [7] extended this work to elevated temperatures up to 110 °C. Gianola et al. [8] performed tensile SRJ tests on free standing Al films with nominal thickness of 150 and 300 nm at room temperature. Due to inherent difficulty in micro-sample preparation and testing, the majority of the micro- and nano-mechanical efforts to measure SRS involve approaches based on nanoindentation [9–12]. In particular, the recent adaptation of SRJ tests to nanoindentation by Maier et al. [13] allowed investigation of the SRS of nanocrystalline nickel and ultrafine grained (UFG) aluminium. The strain rate was changed during the loading cycle of a standard nanoindentation test by varying the \( \frac{P}{P'} \) (rate of load change/instantaneous applied load) and measuring the change in hardness from continuous stiffness mode data. The advantage of this method, in comparison to CSR tests with nanoindentation, is that the results are less affected by thermal drift and creep effects at low strain rates and the rate jumps are accomplished at constant microstructure. These SRJ tests yielded SRS exponent closer to macroscopic compression SRJ tests on the same samples at room temperature. This work by Maier et al. [13] is the first investigation that systematically compares and validates nanoindentation techniques with bulk testing approaches for SRS measurements. This work was recently extended to elevated temperatures on UFG aluminium by Wheeler et al. [14] to extract activation parameters for deformation. The SRS exponents and activation volumes measured as a function of temperature were found to be in good agreement with bulk compression measurements. Wheeler et al. [15] also performed SRS measurements on GaN micropillars using both CSR and SRJ tests to extract the deformation parameters.

The current study aims to extend the repertoire of nanomechanical testing approaches for SRS measurements by demonstrating micropillar SRJ tests on metallic specimens. It also intends to bridge the gap between triaxial stress state testing in small volumes by nanoindentation, and uniaxial testing in conventional tests on bulk samples, by performing uniaxial testing on micropillars. SRJ tests will be performed on micropillars of nanocrystalline nickel film to extract SRS and activation volumes from 25 to 100 °C. The measured parameters will be compared with deformation data reported in the literature. Additionally, the issues surrounding the testing methodology and analysis procedures will be discussed.

2. Experimental

2.1. Sample preparation, composition and microstructure

Electrodeposition of nickel was performed on a polished Cu substrate in an electrochemical cell employing a pure nickel sheet as the counter electrode. The plating bath consisted of 450 g/L Ni\((SO_3NH_2)_2\cdot 6H_2O\), 30 g/L NiCl\(_2\cdot 6H_2O\), 20 g/L boric acid, 0.1 g/L sodium dodecyl sulphate and 2.5 g/L saccharin. This bath is a slight modification of the sulphamate bath used by Zheng et al. [16]. The pH of the solution was adjusted to 3.5 by addition of sulphanic acid. Electrodeposition was carried out galvanostatically at \(-8\, \text{A/dm}^2\) at 60 °C for 8 min by employing a computer-aided potentiostat system.
(PGSTAT 30, Autolab). After deposition, the samples were rinsed in deionized water and dried under argon flow. The films were not polished metallographically to avoid introducing surface damage.

Chemical composition and the thickness of the nanocrystalline nickel film were measured by Glow Discharge Optical Emission Spectroscopy (GDOES) using a JY 5000 RF instrument. Film thickness was around 8 μm. To determine the crystallite size of the electrodeposited Ni films, a BRUKER Discover D8© X-ray Diffraction machine with Cu-Kα radiation at 40 kV/40 mA was employed. Spectra of the specimens were recorded in a 2θ range between 20° and 90° which revealed a strong characteristic Ni-peak [1 1 1] at 2θ = 44.56°. The mean crystallite size, which is the average size of a coherent scattering domain, was calculated by measuring full width half maximum of these peaks and applying the basic form of the Scherrer equation which is valid in crystallite size range from approximately 2 to 100 nm [17,18].

Microstructure of the electrodeposited film was observed with a focused ion beam (FIB) microscope. Specimens were sectioned by FIB using an acceleration voltage of 30 keV and probe current of 1000 pA. The cross-sectioned samples were observed by scanning ion microscope of FIB. For observation, acceleration voltage of 30 keV and the probe current of 5 pA were used. Micropillars with diameters of ~1.5 μm and aspect ratios of ~2.5 were milled using a Ga ion beam in Tescan Vela FIB instrument. The pillars were milled in three sequential stages: coarse milling (30KV, ~5 nA), intermediate milling (30KV, ~1 nA) and final polishing (30KV, ~220pA). The micropillars were imaged using a Hitachi S4800 high-resolution scanning electron microscope before and after compression tests.

2.2. Nanomechanical measurements

Nanoindentation tests were carried out in a UNHT system (CSM Instruments, Switzerland) using a sapphire Berkovich tip for comparison with similar data from literature. Hardness and modulus were measured continuously using the Sinus Mode whereby a small sinusoidal function is superimposed on the primary load signal. For these measurements, load amplitude of 1 mN, sinus oscillation frequency of 10 Hz and maximum load of 100 mN were used. Constant indentation strain rates ranging from $2.5 \times 10^{-3}$ to $2.5 \times 10^{-1}$ s$^{-1}$ were applied by keeping $\dot{P}/P$ (rate of load change/instantaneous applied load) ratio constant. This resulted in loading times for a single measurement varying between 13 and 1400 s. Hardness values corresponding to depth of ~1 μm were considered for analysis in order to provide a consistent comparison between the different strain rates. A minimum of seven indents were performed at each strain rate and the results were averaged.

Micropillar SRJ tests were carried out in an Aleminis in situ, elevated temperature indentation system in a Zeiss DSM 962 SEM. The details of the indentation system have been reported previously [19]. Micropillar compressions, as well as micropillar SRJ tests, were carried out at three different temperatures: 25, 62.5 and 100 °C. The sequence of testing was 100 °C, 25 °C followed by 62.5 °C, so that the initial tests at 100 °C relax the grain boundaries and allow grains to grow to a steady state size distribution. The high vacuum of the SEM chamber (~10$^{-4}$ Pa) prevents sample surface oxidation. Thermal drift at elevated temperature testing was minimized by tuning the tip temperature with the sample surface temperature [20]. All test temperature values
reported in this paper correspond to the sample surface temperatures measured by the calibrated indenter tip. The accuracy of surface temperature measurement and tip temperature tuning was <0.5 °C. Since an intrinsically displacement controlled indenter was utilized for these experiments, the SRJs could be incorporated easily. The strain rate was varied by a factor of 25 from 0.0002 to 0.005 s\(^{-1}\).

A diamond flat punch was used for the experiments. Although diamond indenters are not optimal for elevated temperature measurements on nickel, as reported recently [21], dissolution or reaction of a flat punch is not of concern in micropillar measurements unlike conical tips and for test temperatures up to 100 °C. Six micropillars were tested at each temperature: three for CSR micro-compression and three for SRJ tests.

3. Results and discussion

3.1. Composition and microstructure

Electrodeposited films contain higher amounts of impurities in comparison to vacuum sputtered films. Although the effect of solid solution alloying elements, like tungsten [22], on the mechanical deformation behaviour of nanocrystalline nickel has been of primary interest to the community, the influence of impurities can be significant. For example, segregation of sulphur above 330 °C has been reported to form Ni-sulphide at the grain boundaries resulting in substantial decrease in flow stress [23]. The effect of B and C doping on the mechanical properties has also been discussed [24–26]. These impurities hamper grain growth and render microstructural stability to the grains.

The nominal composition of the nanocrystalline nickel sample as determined from GDOES is reported in Table 1. Nickel electrodeposit was found to be 98.7% (mass %) pure with trace amounts of Al, C, Cu and S. Co concentration was found to be higher (1.2 mass %) than expected due to contamination. Solid solution strengthening effect due to cobalt in nickel matrix is low [27]. For such low concentrations, the effect of Co on strength of electrodeposited nickel can thus be neglected.

XRD measurements using the Scherrer formula estimate the average coherence length of a scattering domain. Microstructural features like grain boundaries, sub-grain boundaries or twins can contribute to this estimation which may lie well below the actual grain size. The mean crystallite size of the deposits estimated from XRD was 27 nm. It should be noted that crystallite size is different from grain size since one grain can consist of several crystallites [28]. However, in case of mechanical deformation behaviour, these microstructural features like low-angle grain boundaries, sub-grain boundaries and twins impede dislocation glide. Therefore, crystallite size has also been widely reported as grain size in the literature for nanocrystalline materials. Apart from the average grain size, the grain shape and distribution also affects the mechanical behaviour. Limitations of XRD measurements include measurement of grain size only in the direction perpendicular to the surface, and no information about grain size distribution [29] and their shape. FIB channelling contrast images (Figure 1) of trenches cut

| Element | Ni     | Co     | Al    | C    | Cu    | S     |
|---------|--------|--------|-------|------|-------|-------|
| Content (mass per cent) | 98.740 | 1.191  | 0.005 | 0.025 | 0.025 | 0.010 |
out from the electrodeposited nickel film showed non-columnar grains. The grains at the surface are larger in comparison to the bulk on account of grain growth due to prolonged exposure to high-energy beams. Since the grains grow during FIB milling as well as during imaging, such images provide a qualitative idea about the grain shape and size distribution.

Microstructural stability is important for the current study on account of elevated temperature testing. Grain growth between different temperature runs and during testing can exhibit anomalous mechanical deformation behaviour that can make interpretation of experimental data difficult. Hence, it was important to ascertain the highest testing temperature so that we can be reasonably sure of absence of grain growth and perform all tests with the same starting microstructure. Previous studies on nanocrystalline nickel have reported appreciable grain growth above 200 °C [16,29–31]. Therefore, we decided to keep the maximum temperature of testing at 100 °C. For direct experimental verification of absence of substantial grain growth, an electrodeposited nanocrystalline nickel sample was annealed at 100 °C for over 24 h. The average crystallite size increased from 27 nm in as-deposited condition to 31 nm for the annealed sample, which is similar to the observations reported by Zheng et al. [16].

3.2. **Micropillar compression results**

Figure 2 shows representative engineering stress–strain curves from CSR micropillar compression results obtained at three test temperatures. The nanocrystalline film exhibits 1% offset yield strength of 1.89 ± 0.05 GPa at room temperature, and the yield strength
decreases with increasing test temperature (1.80 ± 0.09 GPa at 62.5 °C and 1.63 ± 0.09 GPa at 100 °C, measured for 6 micropillars each). It should be noted that the room temperature tests were preceded by 100 °C tests. The engineering stress–strain data obtained at room temperature on this annealed sample were compared with another sample in as-deposited condition. The room temperature results from both samples overlapped nicely suggesting negligible grain growth and no noticeable change in mechanical properties on account of initial testing at 100 °C (Online supplemental data).

An intriguing observation in the engineering stress–strain curves is the apparent strain hardening for micropillar compression results. Nanocrystalline materials do not typically exhibit strain hardening [1], which is attributed to saturation of dislocation density due to dynamic recovery or due to annihilation of dislocations into the grain boundaries [1]. So, the observed strain hardening might be a geometrical artefact. On careful observation of the micropillars before and after compression (Figure 3), it was noticed that the pillars have a taper of 2.5 ± 0.3° (calculated for 18 micropillars) and the bulk of the plastic deformation is accommodated by the top half segment of the micropillar. In situ testing videos obtained during compression also showed the top half deforming the most, with grains rotating and sliding out of the free pillar surface, while the bottom half segment was not greatly affected. Grain boundary sliding was observed in the scanning electron micrographs at the surface of the deformed pillars (Figure 3). The larger grains showed slip traces. The geometric effect of pillar taper and plastic strain localization in the top segment during compression might explain the apparent strain hardening observed in this case. The geometric issue of pillar taper has been addressed by Yang et al. [32] for accurate extraction of elastic modulus from micropillar compression tests. Nevertheless, it is instructive to explore the reason for the observed apparent strain hardening in engineering stress–strain data using some simplistic assumptions.
Figure 3. High resolution SEM images of a micropillar (a) before and (b) after compression to 25% strain at room temperature showing that the top half accommodates the bulk of the plastic deformation. (c) Extensive grain boundary sliding can be observed in the top half of the deformed pillar. Slip traces are observed in the larger grains.
As a rough first approximation to determine the effect of the strain localization in the top segment of the micropillar, engineering stress–strain curve for a particular test run was recomputed by assuming the pillar height to be half of its original height. The true stress–strain curves for the original and reduced pillar heights were also calculated based on the assumption of constant volume and homogeneous deformation. Additionally, the stress–strain curve was calculated for the top diameter after compression. These results are shown in Figure 4. Reducing the pillar height by half increases the overall strain but has minor influence on the strain hardening rate. Increasing the pillar diameter (final diameter after compression > initial diameter) decreases the yield point but does not affect the slope of the stress–strain curve beyond the yield point. Therefore, pillar height and diameter, considered separately, do not seem to affect the strain hardening behaviour of the engineering stress–strain curves. However, the true stress–strain curve for the original pillar height, which takes into consideration simultaneous change in pillar height and diameter, does show significant reduction in strain hardening. For the case of half pillar height, the true stress–strain curve exhibits significant strain softening. From these results, it is clear that the apparent strain hardening observed in engineering stress–strain curves is likely a geometric effect due to strain localization resulting from taper and inhomogeneous deformation throughout the height of the pillar. For the subsequent results reported in this paper, the engineering stress–strain curves have been considered. These CSR microcompression results were used to determine the yield strains in order to design the SRJ tests in the plastic flow regime.

3.3. SRS results
Figure 5 shows the engineering stress–strain curves for the SRJ tests at the three test temperatures. After each jump, the flow stress reached a steady state value rather
quickly and SRJs were sharp with very small transients. The strain rates have been marked on one of the curves to provide an idea about the magnitude and sequence of the rate jumps. The same rate jump sequence and testing methodology was used on all the pillars.

The SRS exponent, \( m \), is the measure of the dependence of change in flow stress, \( \sigma \), as a function of change in applied strain rate, \( \dot{\varepsilon} \), at constant temperature, \( T \):

\[
m = \left[ \frac{d(\ln \sigma)}{d(\ln \dot{\varepsilon})} \right]_T
\]

The SRS exponent, \( m \), can be calculated from SRJ tests using two analysis methods: (a) instantaneously for each SRJ, and (b) from the slope of stress–strain rate data plotted in log–log scale, an analysis often used for SRS determination from CSR measurement data. In method (a), the change in flow stress is calculated from experimental data just before and after the rate jump by ignoring the transients. This method of computation does not depend on the slope of the stress–strain curve in the plastic regime and hence, is independent of strain hardening or softening in the material being tested. However, it is sensitive to any noise present in the data during the jump and on jump transients. On the other hand, the value of \( m \) calculated using method (b) is strongly influenced by the slope of the stress–strain curve. In case of strain hardening behaviour, an average value for the flow stress corresponding to an applied strain rate cannot be ascertained for computing the value of \( m \). Since nanocrystalline materials do not exhibit strain hardening, this has not been an issue with bulk measurements. However, the apparent strain hardening behaviour noticed in engineering stress–strain curves from tapered micropillars precludes the direct use of method (b) on experimental data. Data corrections must be introduced before using this method.

Figure 5. (colour online) Engineering stress–strain curves for the SRJ tests on nanocrystalline nickel micropillars at three test temperatures. Each test comprises five SRJs with the strain rates varying from 0.0002 to 0.005 s\(^{-1}\), by a factor of 25.
To remove the influence of the slope on analysis method (b), a straight line was fitted through the initial and final segments of the stress–strain curves that were compressed at the same strain rate of $0.001\,\text{s}^{-1}$. The fitted segment was shifted in stress axis to result in zero slope $\sigma$–$\varepsilon$ curve so as to subtract the apparent strain hardening (Figure 6). The value of $m$ was then calculated from the corrected data using method (b). This correction uses the assumption of reversibility of the strain rate dependent flow [13] to allow all other variations in the $\sigma$–$\varepsilon$ curve to be subtracted, leaving only the SRS. It allows better statistics to be obtained in comparison to method (a), where the stress needs to be calculated over a very narrow range of strain, to avoid jump transients and apparent strain hardening behaviour from affecting the results. A comparison of values of $m$ determined using different methods for a micropillar tested at 100 °C is shown in Table 2. The results from all three analyses are in good agreement.

In order to compare these results with other techniques, room temperature SRS data obtained from micropillar SRJ tests and nanoindentation CSR tests performed on the same sample have been plotted in Figure 7. The flow stress values from nanoindentation data were calculated by dividing hardness by a factor 2.8 [13]. Nanoindentation CSR hardness values from the current work are lower due to substrate effect [33] as the indentation depth-to-film thickness ratio was around 15%. It should be noted that nanoindentation CSR tests yield higher $m$ values due to influence of thermal drift and creep for lower strain rates [13]. For comparison with literature, nanoindentation SRJ and CSR data from Maier et al. [13] are also shown. Values of $m$ obtained from both SRJ techniques and both CSR measurements show good agreement. The average grain size of the nanocrystalline sample, determined from XRD analysis, used by Maier et al. [13] was 80 nm in comparison to 27 nm in our case.

![Figure 6. (colour online) Raw and corrected experimental data for determination of SRS exponent from engineering stress–strain curve for one of the tests. Values of $m$ were determined instantaneously across the SRJs as well as from the slope of stress–strain rate from the corrected data plotted in log-log scale.](image-url)
A first-order approximation of the number of crystallites being interrogated in micropillar SRJ tests will be instructive before comparison with bulk measurements. The mean crystallite size of the nanocrystalline film is 30 nm. Approximating the crystallites to be cubes with edge length of 30 nm and taking the average dimension of a micropillar into consideration (1.5 μm diameter, 2.5 μm height) results in 163,000 crystallites in a single micropillar. Let us assume that the FIB damage is limited to only the top layer of crystallites exposed to the surface [34]. The percentage of ion beam damaged crystallites is 9% in this case. The grain boundary volume fraction is roughly 20% when the boundary width is assumed to be 1 nm [1] and the crystallites are

| Strain rate jump segment (s⁻¹) | Method (a) on raw data | Method (a) on corrected data | Method (b) on corrected data |
|-------------------------------|------------------------|-----------------------------|-----------------------------|
| 0.001–0.0002                  | 0.026                  | 0.029                       |                             |
| 0.0002–0.0002                 | 0.027                  | 0.030                       |                             |
| 0.002–0.0005                  | 0.022                  | 0.028                       |                             |
| 0.0005–0.0005                 | 0.025                  | 0.026                       |                             |
| 0.005–0.001                   | 0.020                  | 0.027                       |                             |
| Average                       | 0.024                  | 0.028                       | 0.027                       |
| Standard deviation            | 0.003                  | 0.002                       | N.A.                        |

Figure 7. (colour online) Log-log plot of hardness vs. strain rates showing micropillar SRJ and nanoindentation CSR data at room temperature. Nanoindentation CSR hardness values are low due to substrate effect and have been divided by a factor of 2.8 to convert it to flow stress values. For comparison with literature, data from nanoindentation tests by Maier et al. [13] are also shown.

Table 2. Comparison of m-values calculated for one of the pillars tested at 100 °C using method (a) (instantaneous SRS determination) on raw and slope-corrected engineering stress–strain curves. The m-value determined using method (b) (from the slope of stress–strain rate plot in log–log scale) on slope-corrected data is also shown for comparison.
assumed to be grains. Therefore, it can be concluded that sufficient number of crystallites and significant volume fraction of grain boundary are being tested in the present study to obtain averaged values for comparison with bulk measurements.

The apparent activation volume $V_{\text{app}}$ was calculated from SRJ tests using the following equation [14,15]:

$$V_{\text{app}} = \frac{\sqrt{3kT}}{m\sigma_f}$$  \hspace{1cm} (2)

where $\sigma_f$ is the flow stress, $k$ is the Boltzmann constant and $T$ is the absolute temperature. The apparent activation volume is directly related to the plastic deformation and is often used to obtain an idea of the governing rate controlling mechanism(s). The variation in SRS exponent, $m$, and apparent activation volume, $V$, as a function of temperature obtained from micropillar SRJ tests is shown in Figure 8. Literature data [35] on bulk uniaxial tensile SRJ tests performed on nanocrystalline samples of average grain size 29 nm, determined using TEM, is also shown. The values of $m$ and $V$ match reasonably well for both cases. These results are consistent with previous literature on bulk deformation of nanocrystalline nickel that report SRS exponent, $m$, of around 0.02 and activation volume, $V$, in the range of $10^{-20} \text{b}^3$ [1,13,23,35–38]. Activation volumes of $\sim 10 \text{b}^3$ correspond to grain boundary diffusion processes [1].

### 3.4. Apparent activation energy for deformation

For many mechanical deformation processes, multiple deformation mechanisms will be active at any time. If the deformation mechanisms are in series, the mechanism having the highest activation energy will be the rate-controlling mechanism. In case of parallel mechanisms, the one having the lowest activation energy will dominate [39]. Due to stress and temperature dependence of the activation energies, only an apparent activation energy value can be calculated which is devoid of any stress dependence. Traditionally, the apparent activation energy for deformation has been calculated from the slope of log ($\dot{\varepsilon}$) vs. $(1/T)$, particularly in the field of creep testing. This follows from the widely used steady state creep equation that correlates the overall strain rate, $\dot{\varepsilon}$, with the applied stress, $\sigma$, through an Arrhenius formulation:

$$\dot{\varepsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right)$$  \hspace{1cm} (3)

where $A$ is a pre-exponential constant, $R$ is the gas constant and $T$ is the temperature in degrees K. On taking logarithm of both sides, this equation reduces to:

$$\log(\dot{\varepsilon}) = \log A + n \log \sigma - \frac{Q}{RT}$$  \hspace{1cm} (4)

Assuming $(\log A + n \log \sigma)$ to be constant, the slope of $\log(\dot{\varepsilon})$ vs. $(1/T)$ provides the value of $(-Q/R)$. The inherent assumptions are the attainment of steady state strain rates at each test temperature and strain rate values plotted for the same stress levels. This follows from the assumption of constant microstructure in steady state creep regime.

For SRJ tests, the case is slightly different, although some parallels can be drawn to the creep tests. Due to absence of strain hardening in nanocrystalline materials [1], the assumption of constant microstructure can be considered to hold true. Also, the strain
rate remains constant, which can be considered analogous to CSR in secondary state creep tests. The only difference is that the stress values are not the same for the pillars measured at different temperatures. Since flow stress is a strong function of the applied strain rate for nanocrystalline nickel pillars tested, the strain rates can be extrapolated to constant stress values to calculate the apparent activation energy for deformation (Figure 9). This yields an apparent activation energy value of 102.5 kJ/mol, which is close to the boundary diffusion activation energy for nickel (115 kJ/mol) [40]. It should be pointed out that similar apparent activation energy values were also obtained from
bulk compression experiments on nanocrystalline nickel by Kottada and Chokshi [41] from creep measurements and by Li et al. [42] from SRS measurements.

Another approach for calculating the apparent activation energy using the same concept, from hardness values suggested by Sherby and Armstrong [43], involves slight modification of Equation (3) to compensate for the creep stress exponent, $n$, in the exponential term. Taking this logic further and equating $m = (1/n)$, the following equations are obtained:

Figure 9. (colour online) Apparent activation energy for deformation calculated by plotting extrapolated strain rate, corresponding to the same stress level, in log scale vs. $1000/T$. 
\[
\dot{\varepsilon}^{(\Sigma)} = A^{(\Sigma)} \sigma \exp\left(\frac{m}{RT}\right) \quad (5)
\]

\[
\dot{\varepsilon}^{(m)} = A^{(m)} \sigma \exp\left(\frac{mQ}{RT}\right) \quad (6)
\]

\[
\sigma = \frac{1}{A^{(m)}} \dot{\varepsilon}^{(m)} \exp\left(\frac{mQ}{RT}\right) \quad (7)
\]

Figure 10. (colour online) Apparent activation energy values calculated from log (stress) vs. (1000/T) plots as a function of applied strain rates.
\[
\log \sigma = \log \left( \frac{1}{A(m)} \right) + m \log \dot{\varepsilon} + \left( \frac{mQ}{RT} \right) \tag{8}
\]

\[
\log \sigma = B + \left( \frac{mQ}{RT} \right) \tag{9}
\]

where \( B = \log \left( \frac{1}{\dot{\varepsilon}_0} \right) + m \log \dot{\varepsilon} \).

Assuming a constant average value of \( m = 0.02 \), an apparent activation energy value of \( 92 \pm 9 \text{ kJ/mol} \) is obtained over the tested strain rates (Figure 10(a)) that corresponds well with the previously calculated value. Changing \( m \) from 0.014 to 0.026 (values for \( RT \) and 100 °C, respectively) changes the apparent activation energy from 135 to 72 kJ/mol. These values are still in the range for boundary diffusion. It should be noted that the activation energies for nickel for lattice diffusion and core diffusion are 284 and 170 kJ/mol, respectively, quite far off from the values calculated from SRJ tests. The apparent activation energy seems to decrease with the applied strain rate (Figure 10(b)), indicating that more deformation is accommodated by dislocation plasticity at higher strain rates.

Lohmiller et al. [44] reported on the sequence of deformation mechanisms in nanocrystalline Ni with an average grain size of 30 nm. They reported that the deformation behaviour proceeds in the following sequence: (a) elasticity, (b) grain boundary shear and slip, (c) dislocation glide and (d) finally grain growth at large strains. They further stated that the deformation is governed by succession of these different, partly overlapping mechanisms. In case of deformation mechanisms in series, the deformation mechanism that has the highest activation energy becomes the rate controlling mechanism. The apparent activation energy extracted for the deformation should match closely with the activation energy of the rate controlling mechanism in this case [39]. Since the activation energy for slip is very small in comparison to that for grain boundary diffusion and these mechanisms can be considered to be in series, we obtain an apparent activation energy value that matches closely with grain boundary diffusion. These observations are consistent with large volume fraction of grain boundaries present in the sample and extensive grain boundary sliding observed in the deformed pillars.

4. Conclusions

Microcompression SRJ technique has been successfully demonstrated on nanocrystalline nickel. Good agreement was obtained for SRS exponent, \( m \), and activation volume, \( V \), between microcompression and bulk compression SRJ tests from 25 to 100 °C. The apparent activation energy extracted from SRJ tests matched well with grain boundary diffusion activation energy for nickel suggesting it to be the rate controlling deformation mechanism. Electron microscopy of the deformed pillars showed extensive grain boundary sliding and rotation to accommodate the plastic strain. Slip traces were also observed in case of large grains. These observations are consistent with the existing literature. The microcompression testing technique and the analysis methodology described in this paper enable determination of SRS parameters from micro-pillar samples prepared from thin films and coatings as well as site specific small length-scale microstructural features.
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