

Marshall Plan Scholarship Research Report

# Nanoindentation of Ultra-Fine Grained and Single Crystalline Chromium and Tantalum

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# Affidavit

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

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February 18, 2015

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# **Abbreviations and Symbols**

<i>b</i>	Burgers vector
έ	strain rate
A <sub>proj</sub>	projected area
ARB	Accumulative Role Bonding
bcc	base centered cubic
BSE	back scattered electrons
c*	constraint factor
C <sub>f</sub>	frame compliance
cg	coarse grained
C <sub>total</sub>	system compliance
d <sub>G</sub>	average grain size
DSI	depth-sensing indentation
Ε	Young's modulus
EBSD	electron back scattered difraction
ECAP	Equal Channel Angular Pressing
Er	Reduced modulus
fcc	face centered cubic
Н	hardness
h	(indentation) depth
H <sub>0</sub>	macroscopic hardness
h <sub>c</sub>	contact depth
h <sub>el</sub>	elastic depth
h <sub>max</sub>	maximum depth
h <sub>pl</sub>	plastic depth
ISE	indentation size effect
k	Hall-Petch strengthening coefficient
k <sub>в</sub>	Boltzmann constant
m	strain rate sensitivity
nc	nanocrystalline
Ρ	load
S	stiffness
SE	secondary electrons

## Abbreviations and Symbols

SRS	strain rate sensitivity
SX	single crystal, single crystalline
Τ	absolute temperature
T <sub>c</sub>	critical temperature
ufg	ultra-fine grained
ε	strain
ν	Poisson's ratio
τ	shear stress
б <sub>0</sub>	critical flow stress in a single crystal
б <sub>f</sub>	flow stress
б <sub>у</sub>	yield strength

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# **1** Introduction

Nowadays knowledge about materials, their behavior and the underlying physical mechanisms governing them, allows the customizing of material properties for more or less every application. There are for example many different ways to improve or alter the mechanical properties of metals. This is often connected to at least a certain degree of using alloying elements such as it is the case for solid solution or dispersion hardening. Different to that, work hardening is not in need of any alloying system to work, but is otherwise well known to cause embrittlement of the material which is subjected to it. Therefore a subsequent annealing process is usually applied to increase the ductility. The only known technique to increase mechanical properties such as hardness and strength and not in general causing reduced ductility, is grain refinement [1]. This is usually achieved by either applying a fast cooling rate to solidifying melts, or by recrystallization through deformation and heat treatment. A more novel technique leading to a wider horizon in terms of accessible grain sizes and therefor properties and applications is severe plastic deformation (SPD). Before it came up in the early 1990s [2], the only chance to produce ultra-fine grained (< 1000 nm), or even nanocrystalline materials (< 100 nm) was powder consolidation with all its drawbacks such as residual porosity, impurities from ball milling etc.

Since then ultra-fine grained (ufg) and nanocrystalline (nc) materials have been subject to numerous scientific studies focused on revealing their unique properties. Besides the mentioned outstanding strength potential of ufg materials, diverse studies revealed also interesting properties in terms of conductivity, magnetic properties [2], radiation tolerance [3, 4] etc. But one of the most interesting questions which arose was about the deformation mechanisms of such materials. While for face-centered cubic (fcc) materials a significant body of research is available, the knowledge about those of body-centered cubic (bcc) and hexagonal close-packed (hcp) materials is still modest [5]. However, it is currently believed that the well-known kink-pair nucleation mechanism for screw dislocations is, such as for coarse-grained bcc metals as well, the dominant mechanisms of plastic deformation [6].

In order to determine the mechanisms governing the plastic deformation, material properties such as the strain rate sensitivity (SRS) or the activation volume (V\*) are often considered. These are time-dependent and are thus well suited to obtain limiting steps in the process of plastic deformation. These quantities can be determined by different testing methods and especially nanoindentation became the most popular technique to access them. This is due to several reasons such as the ability of probing very small volumes and therefore gaining a large

number of data for limited test sites. The possibility of automatizing the testing procedure as well as the simultaneous measurement of indentation depth and time make it a favorable technique to obtain time dependent values.

Since the difference between coarse grained or even single crystalline materials compared to ufg materials is of special interest, one focus of this work is to compare the mechanism of plastic deformation for these types of microstructures. Another aspect will be the determination and comparison of the hardness of these materials. The single crystalline materials used in this work potentially show further interesting properties such as indentation size-effects (ISE) which will be discussed later in detail. Furthermore these experiments are not only conducted at room temperature, but at several elevated temperatures as well.

## 2 Theoretical Background

## 2.1 Properties and Mechanical Behavior of single crystalline and ultra-fine grained body-centered cubic Materials

Mechanical properties such as hardness, strength and ductility of crystalline materials, such as metals, at a given temperature are governed by different distinctive features. Besides others, these are primarily the chemical composition (i.e. the element or alloy) and the microstructure. Both are affecting the movability of dislocations, which are linear lattice defects and the major source of crystal plasticity, in different ways. When two or more different sorts of atoms form an alloy, solid solutions are built which lead to an elastically distorted lattice of the crystal. The interaction between the lattice's and the dislocation's area of distortion is affecting the movability of the dislocation. However, the microstructure, on which the focus is put in this work, describes the size, shape and arrangement of grains in a polycrystalline material. The boundaries between the grains display severe obstacles for the movement of dislocations [1]. This is obviously the case when different grains with grain boundaries are present, but is not the case for single crystalline material, which consist only out of a single grain. The properties of a single crystal are thus mainly governed by the mentioned chemical composition and additionally the density of dislocations.

#### 2.1.1 Hardness and Yield Strength

Upon the most used parameters for the choice of materials is the hardness. This is due to the fact that it can be easily obtained by cheap standardized measuring procedures such as microhardness testing as for instance Vickers, Brinell or Rockwell hardness testing. Hence it allows a fast comparison of different materials which were tested at similar conditions [7]. The mathematical definition of the hardness is the ratio between the maximum load of an indenter  $P_{max}$  and the area A of the created indent after a specified dwell time Eq. (1)

$$H = \frac{P_{max}}{A} \tag{1}$$

It needs to be said that different techniques of hardness testing observe different projected areas based on their measurement principles. Whereas conventional microhardness testing methods such as those mentioned above are usually equipped with an optical microscope to determine the residual inprint of the indent after unloading, modern nanoscale testing techniques such as nanoindentation (see chapter 2.4) measure load displacement curves and derive the projected contact area from the unloading slope.

Another commonly used parameter describing the strength of a material is the yield strength  $G_y$ . This is the stress which needs to be applied to introduce plastic flow, or, more specifically, to move dislocations. The flow stress  $G_f$  is the strength of a material at a given strain. Both are commonly determined by tensile or compression yield tests. The mentioned parameters are correlated by the constraint factor c\*such as shown in Eq.(2) [8].

$$c^* = \frac{6_f}{H} \tag{2}$$

In practical use, a value of  $c^* = 3$  is often applied, although the value is governed by the nature of deformation. The higher the ratio of Young's modulus to flow stress, the more plastic is the character of the deformation. To take that into consideration, Johnson [9] suggested the distinctions in Table 1:

Та	ble 1 : Overview of constraint factors for diff	erent characters o	f deformation	
•	Fully elastic deformation		< C <b>* &lt;</b>	1.07
•	Elastic and plastic deformation	1.08	< C* <	2.80
•	Fully plastic deformation	2.80	< c* <	

#### **Microstructural Influence**

Grain refinement of crystalline materials leads to an enhanced flow stress. This behavior was, among others, investigated by Hall and Petch in the 1950s [10, 11]. Their proposed mechanism explains this behavior based on dislocation pile ups at grain boundaries. These act, due to the orientation mismatch between the grains, as obstacles for dislocation movement. The relation between the flow stress and the grain size was found as shown in Eq.(3) :

$$6_y = 6_0 \cdot \frac{k}{d_G^2},$$
(3)

where k is the strengthening coefficient and  $G_0$  is the friction stress which includes contributions from solutes and particles but not from dislocations [12]. Since the hardness and strength of pure metals is mainly caused by microstructure and dislocation density, Eq.(3) leads to a considerably increased hardness and strength for ufg polycrystalline materials, compared to their chemically equivalent single crystalline or coarse grained counterparts. This is especially true when the measurement length scale is above a certain value, where no size effect (see chapter 2.1.4) for sx and cg material is occurring. While this equation was confirmed countless times for a broad variety of materials, its validity in the lower end of the accessible nanocrystalline regime (d<sub>G</sub> ≈ 10nm) was discussed over the last decades [13, 14, 15]. For this grain size regime, a strength plateau or even a softening was reported. However, this is not of concern for this work, since the average grain size of the used samples is situated well above that (see chapter 3.5).

Cubic crystal lattices, such as bcc, show in general anisotropic behavior with a 90° symmetry. This means that materials properties of single crystals are changing with the lading angle, but reach the same values for steps of 90°. For randomly distributed grain orientations in polycrystalline materials, this effect is obviously compensated.

#### **Temperature Influence**

A single crystal containing no further defects (dislocations, impurity atoms, grain boundaries, etc.) possesses a specific flow stress, the intrinsic flow stress. When a dislocation moves, the atomic bonds to one adjacent crystallographic plane are stretched, those on the opposite plane are pushed together. This mechanisms demands energy, respectively stress. At a certain stress level the atomic bonds of the dislocation plane switch and the dislocation moves forwards by one atom spacing. The stress level needed to overcome this potential is called "Peierls-stress" [1].

For crystal structures which possess dense packing, such as fcc and hexagonal systems, the contribution of the Peierls-stress to the entire flow stress is minor. For bcc sx and cg materials, however, the Peierls-stress is a major contributor to the flow stress at low temperatures. On the other hand, the influence of this Peierls stress for polycrystalline bcc material is less pronounced compared to bcc sx material due to the contribution of grain boundary strengthening to the overall flow stress. According to that the flow stress of bcc materials is often separated in an athermic part, which is primarily governed by microstructure and solid solution hardening (for non-chemically pure materials), and an strongly temperature dependent thermal part which is mostly the Peierls-stress.

If the stress applied is not sufficient to enable dislocations to overcome obstacles and move, thermal activation can provide the required energy. The probability p of a dislocation to overcome an obstacle by means of thermal activation is shown in Eq.(4).

$$p = exp\left(-\frac{Q - 2 \cdot \lambda \cdot b \cdot d^* \cdot \tau^*}{k \cdot T}\right)$$
(4)

The numerator in the exponential function represents the energy gap between obstacle potential Q and available work done by the movement of a dislocation.  $\lambda$  is the half obstacle spacing, b the dislocations Burgers vector, d<sup>\*</sup> the average width of the obstacle potential and  $\tau^*$  is the effective stress on the dislocation. k is the Boltzmann constant and T the absolute temperature.

If the Peierls-stress is assumed to be a special kind of barrier, this mechanisms is decreasing its share to the flow stress when increasing the temperature. Therefore the Peierls-stress is also referred to as "thermic part" of the flow stress and vanishes finally at a material dependent critical temperature called  $T_c$  [1]. An overview of this behavior for bcc sx and ufg material is shown in Fig. 2.1 for the case of tungsten. For the single crystal the Peierls-stress, G', is strongly contributing to the overall flow stress at lower temperatures, though it vanishes at a strain rate dependent critical temperature,  $T_c$  ( $\dot{c}$ ). Above this temperature, the single crystals flow stress is completely governed by its athermic part,  $G_{a-sx}$ . Because of the grain boundary strengthening, the Peierls-stress plays only a minor role for the flow stress in terms of the polycrystal. This is the reason why it is assumed to only possess an athermic part,  $G_{a-ufg}$ , with strain rate sensitivity that is caused predominantly by grain boundary mechanisms and increases with temperature [16].



Fig. 2.1: Flow stress dependence of sx and polycrystalline tungsten as an example for the temperature dependence of bcc polycrystalline and single crystalline or coarse grained metals [16].

#### 2.1.2 Young's Modulus

Hook's Law is relating mechanical stress 6 with strain  $\varepsilon$ . The relation factor used is the materials constant Young's modulus E. This is a direct consequence of the interaction between the atoms in the crystal lattice and the assumption that a small displacement of atoms from its lattice position is reversible and the force needed to do so is in a linear relation to the displacement. It can be interpreted as the resistance of a material to elastic deformation.

#### **Microstructural Influence**

As mentioned for the strength above, the elastic properties of sx cubic materials are in general anisotropic as well. Otherwise there is no major influence of the microstructure on the Young's Modulus.

#### **Temperature Influence**

The Young's Modulus is corresponding to the curvature of the potential versus atomic spacing relation. For each temperature a certain equilibrium bonding distance between the atoms exists, which is increasing with temperature. Higher distances are linked to smaller curvatures of the potential curve and thus to lower values of the Young's modulus. This relation is shown in Fig. 2.2. An overview of the temperature dependence of Young's modulus for some metals is given in Fig. 2.3



Fig. 2.2: Dependence of potential energy between two atoms on the bonding distance. Two different temperatures ( $OK \& T_2$ ) and corresponding bonding distances  $r_0$  are shown [1].



Fig. 2.3: Temperature dependence of Young's Modulus for different base centered cubic metals [17].

#### 2.1.3 Strain Rate Sensitivity and Activation Volume

Some materials' flow stress shows a significant dependence on strain rate they are subject to. This behavior can be described with a power-law relation such as shown in Eq.(5). Here  $\mathcal{G}_f$  is the flow stress, K is an auxiliary variable,  $\dot{\varepsilon}$  the strain rate and m the strain rate sensitivity. By reassembling Eq.(5) with respect to m the mathematical expression for the SRS can be found such as shown in Eq.(6) [18].

$$6_f = K \cdot \dot{\varepsilon}^m \tag{5}$$

$$m = \left(\frac{\partial \ln 6}{\partial \ln \dot{\varepsilon}}\right)_T \tag{6}$$

The reason for the appearance of SRS can be explained by time dependent processes such as the movement of. Thermally activated mechanisms can be used to explain the influence of temperature and differences between bcc and fcc materials. As shown in Eq.(4) the probability of a dislocation to overcome an obstacle by thermal activation is increased by elevating temperature. Furthermore P from this equation might be interpreted as the chance to overcome obstacles for each (temperature caused) oscillation of the atom from its lattice position. Therefore it is obvious that due to a higher strain rate the amount of possible attempts in a certain time to overcome obstacles is decreased, which directly leads to a higher flow stress [1]. Especially the double-kink mechanism which thermally enables the movement of screw dislocations, is believed to have a major share on the plastic flow properties of bcc materials.

Opposite to fcc, bcc metals show a decreasing SRS with decreasing grain size. An overview of this trend for different bcc metals in the nc, ufg and coarse grained regime is shown in Fig. 2.4a (including Tantalum) and in Fig. 2.4b (including Chromium). Whereas Fig. 2.4a shows results from tensile (T) and compression (C) tests received from ECAP and partially cold rolled specimens, those from Fig. 2.4b were obtained from electro deposited samples by nanoindentation. Though the production route as well as the testing procedure are different, the evaluated data follow the same trend of decreasing SRS with decreasing grain size in the ufg and coarse grained regime. However, it needs to be mentioned that for the lower end of accessible grain sizes – a few 10nm – this trend is discontinued. Some investigations reveal a steep increase of SRS with decreasing grain size in this regime [19]. However, since the samples used in this work are ufg (>100nm) this is not for any further concern for our studies.

Though the SRS is already a major indicator for the governing mechanism of plastic flow, there is another distinctive variable which is often used in literature: The activation volume V\*. It is defined as shown in Eq.(7).

$$V^* = \sqrt{3} \cdot k_B \cdot T \cdot \frac{\partial \ln \dot{\varepsilon}}{\partial 6} \tag{7}$$

Here,  $k_B$  is the Boltzmann constant and T the absolute temperature. This number is usually divided by the cube of the Burgers vector  $\overline{b}$ , which leads to the approximate amount of unit cells which contribute to the rate limiting step of plastic deformation.



Fig. 2.4a.: Overview of the grain size dependence of the strain rate sensitivity for different bcc metals including Tantalum [6]. Production route: ECAP and partially cold rolling; testing procedure: tensile or compression tests. b.: including Chromium [19] production route: electrodeposition; testing procedure: nanoindentation.

For both, the strain rate sensitivity and the activation volume, one can imagine that for single crystalline and coarse grained materials which are supposed to show an indentation size effect

for the hardness, this might influence these values and make them, in terms of nanoindentation depth dependent. Maier et al. [20] could show that this is in fact only true for the activation volume, which is increasing with indentation depth till a large share of the macroscopic hardness is reached, but not for the SRS which was found independent of the indentation depth. Keeping the constant SRS in mind, this behavior is comprehensible with the use of Eq.(27), as explained later.

#### 2.1.4 Size Effect

Besides the overall differences in terms of strength for different grain sizes, there is one unique feature of coarse grained and single crystalline materials: Their yield strength and hardness are size dependent. This means that with decreasing indentation size the mentioned numbers increase. One of the first comprehensive explanations for that phenomena [21] revealed that the high strain gradients in small indents lead to a high number of geometrically necessary dislocation which harden the sample. This is shown in a schematic way in Fig. 2.5, where the geometrically necessary dislocations form closed loops with Burgers vector perpendicular to the plane of the surface. Such length scale dependent behavior can not only be obtained with nanoindentation (ISE), but also with other mechanical testing procedures such as micropillar compression [22] or tensile testing [23].



Fig. 2.5: A schematic description of geometrically necessary dislocation building circular loops with Burgers vector perpendicular to the plane of the surface to realize the ideal geometry [21].

Nix and Gao [21] also found a law based on their strain gradient plasticity theory which allowed them to accurately model the size effect measured by means of nanoindentation:

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}} \tag{8}$$

Here, H is the hardness at a certain indentation depth h and  $H_0$  is the macroscopic hardness of the material.  $h^*$  is an internal length scale which describes the increase of hardness with shallower indentation depths and is depending on the chemical composition of the material and its microstructure.

## 2.2 **Production of bulk ultra-fine grained materials**

#### 2.2.1 Technique overview

Basically, there are two possible routes for the production of ultra-fine grained or nanocrystalline materials. These are namely the top down route, which means the refinement of an already existing more or less coarse grained microstructure, most often by means of severe plastic deformation (SPD), and the bottom up route, using techniques where nano-sized powders, produced by sputtering or ball-milling, are consolidated. The later one is chosen particularly when the aimed grain size is below a certain limit accessible with the techniques of SPD. Table 2 shows a summary of commonly used methods for the production of bulk ufg materials according to [2, 19, 24].

 Table 2: A summary of commonly used methods for the production of bulk nanostructured materials separated in top-down and bottom up techniques

top-down methods of severe plastic deformation

- High Pressure Torsion (HPT)
- Equal Channel Angular Pressing (ECAP)
- Accumulative Roll Bonding (ARB)

- bottom-up methods of consolidation
- Electrodeposition
- Pressing and Sintering

#### 2.2.2 High Pressure Torsion

Similar to other SPD techniques, HPT introduces a high amount of plastic deformation to the sample in order to refine the grain structure. This is achieved by torsional movement of one out of two plungers (see Fig. 2.6) while applying a high hydrostatic pressure onto the usually disc-shaped sample. This is located in a cavity formed by the dies of the plungers. In theory it

#### 2 Theoretical Background

is not absolutely necessary that the sample thickness decreases during the deformation process. It is only needed to assure a constant traction between the sample and the rotating plunger to avoid slipping and therefore insufficient deformation. This would, for example, work with perfectly constrained deformation conditions for the sample (Fig. 2.6a). In practical use, the deformation conditions are only partly constrained and to guarantee a steady traction between the sample and the plungers, it is feasible to use a sample with a higher thickness than the dies are able to accommodate. This leads to an emerge of excess material at the beginning of the deformation process such as it is shown in Fig. 2.6b.

Due to the rotation of the plunger, the shear strain in the sample is not equally distributed, but a function of the radius as shown in Eq.(9) where n is the number of revolutions, t the thickness of the specimen and r the radial position on the sample. Although this is only absolutely accurate for the idealized HPT process, it allows an estimation of the shear strain in a non-idealized sample as well.

$$\gamma(r) = \frac{2 \cdot \pi \cdot n}{t} \cdot r \tag{9}$$



Fig. 2.6: Schematic representation of a high pressure torsion setup with mounted sample. (a) Idealized with perfect constraint conditions and (b) practical with partially constraint conditions. Adapted from [25].

The Institute of Metal Physics in Sverdlovsk investigated intense deformations on different metallic alloys and substituted Eq.(9), which only considers shear strain, with a formula (Eq.(10)) providing the true accumulative strain  $\epsilon$  [26].

$$\varepsilon(r) = \ln\left(\frac{2\cdot\pi\cdot n}{h}\cdot r\right) \tag{10}$$

As a consequence, the grain size in the center of rotation should be quite unaffected and is decreasing with the radius or more specifically with strain. This is true till a certain material and processing parameter depended minimum grain size is reached at high strain levels. This typical behavior is shown in Fig. 2.7 for austenitic steel and different numbers of rotation regarding the HPT process. At a certain radial point, the hardness (which is an indicator for grain size due to grain size hardening) reaches a maximum level and is not increasing with the radius (strain) anymore.



Fig. 2.7: Function of microhardness to the respect of the radius of the sample measured on austenitic steel for different numbers of rotation [25].

Though it needs to be mentioned that some authors were not able to detect a significant decrease of hardness when approaching the center of their disc-shaped HPT specimens [27, 28] Pippan et al. [25] is providing possible explanations for the disappearance of an only slightly deformed sample center which, are summarized in Table 3.

Table 3 : Different reasons for the real and only seemingly disappearance of a only slightly deformed center of the HPT specimens

#### actual disappearance

- Additional compressive deformation caused by the loading of the plunger
- A gap between the centers of rotation for the upper and the lower plunger
- Badly aligned axes of the plungers

#### seeming disappearance

- Hard detectability of small regions with microhardness testing
- Sample preparation (badly positioned center cut for cross section measurements)\*
   \* not [25]

2.3 Microhardness

# These are a group of widely used techniques to observe the hardness while penetrating the sample in a depth of several micrometers. This means that features in materials which are below a certain size cannot be measured independently from other parts of the microstructure. However, it allows a precise measurement of the average hardness of the microstructure present in the sample.

A typical measurement procedure for microhardness testing looks as following: Shock-free loading of the specimen, load holding for a specific amount of time, releasing the load and optically measuring the residual plastic projected area of the indent. A complete result of such tests does not only include the calculated number (load divided by the area, see Eq.(1)) but also the measurement technique, the applied load and for not standardized dwell times these as well.

For the Vickers hardness a diamond pyramid with a square cross section and an opening angle of 136° is used as indenter. The projected diagonal lengths  $d_1$  and  $d_2$  of the residual indent are measured by means of light microscopy and are averaged to the variable d. In Eq.(11) d and the applied load P are linked by a together to determine the Vickers hardness [29].

$$HV = 0.189 \cdot \frac{P}{d^2} \tag{11}$$

## 2.4 Nanoindentation

In the last decades the popularity of nanoindentation techniques increased dramatically for different reasons. Besides the unique possibility of testing very thin films, it is primarily the ability to determine a wide variety of mechanical properties such as Young's Modulus, hardness, creep and relaxation behavior, and many more, in the deep sub-micron regime [30]. As for the microhardness testing, several different indenter shapes, such as Berkovich, spherical, Cube Corner, and conical are used. However, since the experiments of this work where all carried out with Berkovich indenters, the following explanations will be focused on this type.

Nanoindentation is referred to as depth-sensing indentation (DSI). This means that during the process of indentation the penetration depth and the corresponding load are continuously recorded, which leads to load displacement curves such as shown in Fig. 2.8. These are the very basis of every DSI type analysis. Instead of any optical or electron-microscopic measurements of the projected indentation area after the indentation, as it is typical for microhardness testing, is derived from the recorded depth and the known indenter geometry. Since many materials, but especially ceramics and metals, show a significant elastic recovery when unloading, there is a need to specify the different depths which can be measured and particularly the depth which is used to calculate the projected indentation after unloading. The maximum reached depth consisting of an elastic and a plastic part is called  $h_{max}$ , the elastic depth  $h_{el}$ , the plastic depth  $h_{pl}$ . When the indenter penetrates the the sample, the surface is bending away in such a way that the actual contact depth  $h_c$  is smaller than the maximum depth in the load displacement curve.  $h_c$  is derived from the maximum depth and the unloading curve, see chapter 2.4.1.



Fig. 2.8: Typical load displacement curve including the loading, holding and unloading part as well as the most important displacements.



Fig. 2.9: Schematic illustration of the different displacements for a surface under load (black line) and after the unloading (grey line)

#### 2.4.1 Load Schedules

As discussed in chapter 2.1.3, the materials hardness and strength are to a certain degree influenced by the strain rate at which the sample is loaded. Therefore it is obvious that in order to enable the comparison of results, the strain rate needs to be kept constant. Basically there are two different options. The first one is two use static experiments were during the loading  $\dot{P}/P$  is held constant as proposed by [31] and shown in Eq.(12). Here P and  $\dot{P}$  are the loading and the rate of loading respectively. The other option is to hold just the loading rate constant at a certain level which leads to a quasi-static strain rate. For the latter one, the strain rate can be again calculated with Eq.(12).

$$\dot{\varepsilon} = \frac{\dot{P}}{P} \tag{12}$$

Since the unloading part of nanoindentation experiments is fully elastic, it is possible to unload at a certain force, gaining an unloading curve for the determination of the stiffness, and load again. This cyclic procedure leads to several hardness and Young's modulus versus depth couples per indent. The different peak loadings can be calculated by Eq.(13) were  $P_n$  is the peak load at a certain cycle number n,  $P_{max}$  is the maximum peak load, N the overall cycle number and q a spreading factor [20].

$$P_n = P_{max} \cdot \frac{q^{n-1}}{q^N} \tag{13}$$

By combining Eq.(12) and (13) the quasi static strain rate can be determined only depending on loading time  $t_{load}$ , spreading factor and the share of unloading a. This means that for all cycles, though they have different peak loads, the strain rate is equivalent.

$$\dot{\varepsilon} = \frac{q+a+1}{q \cdot t_{load}} \tag{14}$$

#### 2.4.2 Determination of Hardness and Young's Modulus

Nanoindentation experiments provide primarily the load-displacement curves as output data. In the past there where different approaches to use these to determine the mechanical properties of the samples material. In 1992 Oliver and Pharr [32] suggested a procedure which instead of assuming a linear unloading curve, uses a power function to fit it.

$$P(h) = A \cdot (h - h_f)^q \tag{15}$$

A, hf and q are fitting parameters. The stiffness  $S_{total}$  of the sample frame combination is obtained by differentiating Eq.(15) with respect to h and setting h equals  $h_{max}$  such as shown in Eq. (16).

$$S_{total} = \frac{dP}{dh} = A \cdot q \cdot (h_{max} - h_f)^{q-1}$$
(16)

In order to separate the stiffness of the machine and the sample itself, the frame compliance  $C_f$  is subtracted from the total compliance  $C_{total}$ , which is the inverse of the overall stiffness  $S_{total}$ . This approach (Eq.(17)) provides the stiffness S of the sample.

$$S = \frac{1}{C_{total} - C_f} \tag{17}$$

The elastic deformation around the indenter tip  $h_s$  is a function of Pmax, S and a variable called  $\varepsilon$  ( $\varepsilon_{Berkovich} = 0.75$ ) taking the tip geometry into account (Eq. (18))

$$h_s = \varepsilon \cdot \frac{P_{max}}{S} \tag{18}$$

The contact depth is calculated by subtracting  $h_s$  from  $h_{max}$ . Combining this with Eq. (18) leads finally to the formula (Eq.(19)) which is commonly used to determine the contact depth from nanoindentation experiments.

$$h_c = h_{max} - \varepsilon \cdot \frac{P_{max}}{S} \tag{19}$$

To evaluate the contact area  $A_c$  from the contact depth, it is crucial to know the exact relationship between these two numbers, the so called area function. For this task Oliver and Pharr [32] proposed an approximation by means of a polynomial equation (Eq.(20)) in which  $C_1$  to  $C_9$  are the coefficients. For the sake of simplicity in practice usually only the first three terms are used. The error caused by skipping the last six terms is believed to be less than the inaccuracy of the area function calibration (see chapter 2.4.3).

$$A_{c}(h_{c}) = C_{1} \cdot h_{c}^{2} + C_{2} \cdot h_{c} + C_{3} \cdot h_{c}^{\frac{1}{2}} + C_{4} \cdot h_{c}^{\frac{1}{4}} + \dots + C_{9} \cdot h_{c}^{\frac{1}{128}}$$
(20)

Finally, the hardness can be calculated as the quotient of the maximum load and the calculated contact area which leads to Eq. (21).

$$H = \frac{P_{max}}{A_c} \tag{21}$$

The reduced modulus  $E_r$ , which is a property of the sample and the indenter, can be obtained by Eq.(21).  $\beta$  is a geometry factor which takes into account that the Berkovich indenter tip is not a body of revolution ( $\beta_{Berkovich} = 1.034$ ).

$$E_r = \frac{\sqrt{\pi}}{2 \cdot \beta} \cdot \frac{S}{\sqrt{A_c}} \tag{22}$$

Since the contact between sample and indenter tip is very similar to a series of springs with a certain stiffness, the relation between reduced modulus  $E_r$ , the modulus of the indenter  $E_i$  and the sample's modulus E, is very close to such equations as well. Only the lateral contraction needs to be further taken into account by the Poisson's ratio of the indenter material  $v_i$  and of the sample material v.

$$\frac{1}{E_r} = \frac{1 - v_{i\,i}^2}{E_i} + \frac{1 - v^2}{E}$$
(23)

#### 2.4.3 Calibrations

As a consequence of the dependency of both, hardness and Young's modulus on the frame compliance and the area function, the need for a precise calibrations of both values arises. In order to do so a material with isotropic mechanical properties is used for the calibration indents. Commonly used is fused silica with a hardness of 8.85 GPa, a Young's modulus of 69.6 GPa and a Poisson's ratio of 0.17 [33]. Moreover, fused silica shows only a very little inclination to build "pile-ups" (chapter 0) which falsify results when not corrected. Although recent publications [34] report that the area function measured on fused silica is not an inherent property of the tip alone but rather of the fused silica as well, it still stays a very suitable reference material.

For the actual calibration about 100 indents with different loads and therefore different depths are made. Since the mechanical properties hardness and Young's modulus are well known for

fused silica, one can calculate the area function for different loads using Eq. (21) and Eq. (22). By the use of a least square method the frame compliance is varied till a minimum mismatch between the results from the two mentioned equations is reached.

Likewise is the procedure for the area function determination: A least square method is again used to obtain a minimal mismatch between  $A_c$  derived from Eq. (21) and Eq. (22), this time varying the coefficients of the first three terms of Eq. (20).

# 2.4.4 Determination of the Strain Rate Sensitivity and Activation Volume

There are several different methods to obtain SRS with nanoindentation. These are mainly strain rate jump tests [6], which apply different distinctive strain rates during one indentation cycle. The constant strain rate method (CSR) proposed by Lucas [31] is based on several indents with different but constant strain rate. And the constant load (CL) method suggested by Mayo et al. [35] uses relaxation during a constant load segment to obtain the needed hardness and strain rate data. Since for the strain rate jump test special equipment is required and for the CSR method already problems have been reported from the past with the used setup, especially arising from issues with very low strain rates, the experiments carried out in this work are all CL method based. Thus this chapter is also focused on this approach to determine SRS.

The basic idea of the CL method is to obtain time dependent hardness numbers and corresponding strain rates due to the creep of the material during a constant load segment at maximum load. This results in a major difference compared to the other techniques mentioned above. Namely the continuous, instead of discontinuous, sets of hardness and strain rate data. The hardness for nanoindentation experiments was already determined in Eq. (21). A<sub>c</sub> is a function of  $h_c$  (Eq.(20)), which is increasing over time as a result of the creeping material. Hence, the hardness becomes a time dependent number as well. The strain rate  $\dot{\epsilon}$  on the other hand is defined as shown in Eq. (24). Here,  $h_a$  is the absolute depth consisting of a time dependent part  $h_r$  and the depth  $h_0$  reached during the loading of the indenter right before the holding segment starts (Eq.(25)),  $\dot{h}_a$  is it the derivation of  $h_a$  with respect to time required to calculate the strain rate.

$$\dot{\varepsilon} = \frac{\dot{h_a}}{h_a} \tag{24}$$

$$h_a(t) = h_r(t) + h_0$$
 (25)

Different to usual nanoindentation tests which are targeted on evaluating hardness and Young's Modulus, experiments with long dwell times often lead to a considerable depth gain by creeping.  $h_s$  calculated with Eq.(18) using the slope of the unloading curve gives the accurate number for the end of the holding segment, whereas  $h_s$  for the start of it is slightly smaller. However, this is a systematic drawback of this method which can only be avoided by using constant stiffness measurement (CSM) techniques. Therefore, the whole range of h(t) has been subtracted by the same  $h_s$  calculated from the unloading slope to obtain a quasi-contact depth  $h_a(t)$ .

It is common practice to fit the received depth versus time data [36, 37]. This simplifies the differentiation with respect to time which is needed for the calculation of  $\dot{h_a}$ . The fitting was eventually done according to Eq. (26).

$$h_a(t) = a \cdot (t-b)^c + d \cdot t \tag{26}$$

In Fig. 2.10 an illustration of the original raw data of a nanoindentation experiment as well as the related fitting curve are shown. It is evident that the creep rate is decreasing over the dwell time, which provides the needed range of different strain rates for later evaluation. This makes finally the SRS for every couple of hardness and strain rate assessable with utilizing Eq.(6).



Fig. 2.10: Illustration of the time dependent part of the creep curve  $h_a(t)$  and the related fit. Furthermore, the plot is schematically separated into Stage A and B.

Owing to the mentioned continuous data of hardness and strain rate, there is also not one SRS but rather as many as hardness and strain rate data couples. This leads to the question of comparability of the measured SRS' by different techniques. Recently, there are two major approaches. Peykov et al. [36] suggested to separate the creep curve into two distinctive regions, namely stage A and B (see Fig. 2.10) and calculate an average SRS for both. This idea is primarily driven by the assumption that stage B might be stronger influenced by drift issues than it is stage A and that the received m-values from stage A where fairly consistent with those obtained by discontinuous methods. Opposite to that, Maier et al. [38] propose to interpret the different values as dependency of the SRS to the flow stress. Both approaches will be involved in the calculation and the following discussion, see chapters 4.4.2.

In order to calculate the SRS a slight alteration of to Eq. (7) is used. Since the SRS and the hardness are already known, Eq. (8) is a practical approach in finding the activation volume. Since the flow stress needs to be derived from the hardness, it is necessary to estimate the constraint factor, which was finally determined as 2.8 for all samples.

$$V^* = \sqrt{3} \cdot k_B \cdot T \cdot c^* \cdot \frac{1}{m \cdot H}$$
<sup>(27)</sup>

#### 2.4.5 Analysis of the Indentation Size Effect

As mentioned in chapter 2.1.4, the ISE is only pronounced in coarse grained or sx materials. In Fig. 2.11a three hardness versus depth curves showing a clear ISE are plotted for the single crystalline bcc metals tungsten, molybdenum and niobium.

For the actual evaluation of the ISE the model of Nix and Gao is used (Eq.(8)). Since the hardness values H at certain depths h are known, the macroscopic hardness  $H_0$  as well as the internal length scale  $h^*$  can be computed. For that task the original equation is rewritten to Eq.(28) which is obviously linear and thus offers the possibility of using linear regression methods.

$$H^2 = H_0^2 + H_0^2 \cdot h^* \cdot \frac{1}{h}$$
(28)

With the y-interception of the regression line  $H_0$  can be determined which is also required to calculate  $h^*$ . The gained data are usually shown in a so called Nix-Gao plot where the ordinate is  $H^2/H_0^2$  and the abscissa is the reciprocal value of h. This is to enable a direct display of  $h^*$  via the slope of the regression line (Fig. 2.11b)



Fig. 2.11 (a) shows an overview of the size effect measured on different bcc single crystals. Namely Tungsten, Molybdenum and Niobium. (b) shows the relating Nix-Gao plots [16].

Of special concern for the interpretation of the gained data is the fact that the ISE is not every time easily distinguishable from other effects. Fischer-Cripps [30] reports of several non-ISE related influences observed which can really, or only seemingly increase the hardness of a material at shallow depths and might be misinterpreted as ISE (Table 4).

Table 4 : Summarization of different reasons to obtain an actual or only and seeming increase of hardness values at shallow indentation depths.

#### actual hardness increase

- Indentation Size Effect
- thin oxide layer on the surface
- strain hardening from preparation

### 2.4.6 Incipient Plasticity – "Pop-Ins"

The load displacement curves of nanoindentation tests carried out on well-polished and nondeformed materials (e.g. fully annealed or single crystalline materials) show a remarkable feature. The transition between purely elastic to plastic deformation is accompanied by a depth excursion of the indenter while the load keeps constant in a load-controlled test. The so called "pop-in" marks the onset of plasticity, or, put differently, the moment where dislocation start to move. A typical load displacement curve for such a behavior is shown in Fig. 2.12.

- seeming hardness increase
- bad area function
- friction between indenter and surface



Fig. 2.12: Schematic illustration of a typical load displacement curve of a load controlled test, including a popin event. The ranges of the elastic as well as of the plastic part (separated by the pop-in excursion) are shown.

It has been reported numerous times that regarding to contact mechanical considerations the shear stress sustained before yielding is in the order of the theoretical shear strength [39]. Furthermore the very small probing volumes of nanoindentation experiments are often assumed to be free of dislocations and other sorts of defects. Taking these thoughts into consideration, it seems feasible to attribute homogeneous dislocation nucleation (in particular the formation of a closed loop) to the pop-in event as it was suggest among others by Chiu [40]. First doubts to this theory where mentioned by Mason et al. [41] who found higher rate and temperature dependencies (lower activation energies and volumes) than expected for homogeneous dislocation nucleation. A current report [42] obtains proper accordance of the theory of homogenous dislocation nucleation for small tip radii (<210nm), but not for larger ones. Consequently, it is supposed that for very small volumes the homogenous dislocation nucleation might govern the incipient plasticity, whereas for larger ones the activation of already existing dislocation might be predominant. This is underlined by Fig. 2.13 in which the cumulative probability of pop-in events versus the load is displayed for radii ranging from 60 to 759nm. While (a) shows a comparison with a prediction (solid line) only based on homogenous dislocation nucleation, (b) shows a new prediction involving activation of already existing dislocations as well, which gives a much better fit.



Fig. 2.13: Comparison of measured and predicted cumulative probability of pop-in events for (a) a model based only on homogenous nucleation of dislocations and (b) for a model including the activation of preexisting dislocations as well [42].

For the analysis of the incipient plasticity data gained from nanoindentation, usually the assumption is made that the contact between indenter tip and the surface of the sample can be approximated with Hertz' contact relation between a sphere and a flat surface. This is not only assumed for actual spherical, but also for Berkovich indenters with a rounded tip [43]. The equation for the depth dependence of the load is shown in Eq.(29).

$$P = \frac{4}{3} \cdot E_r \cdot R^{1/2} \cdot h^{3/2}$$
(29)

P is the load,  $E_r$  the reduced modulus of the contact, R the tip radius and h the elastic depth. By fitting the elastic part of the loading curve, either the tip radius can be estimated from a known reduced modulus (which was done in this work) or vice versa. To trigger the depth recording of the nanoindenter, a load of 0.05 mN is required. For logical reasons the load data start at this number as well. Nevertheless, the exact depth at this load, which is assumed to be higher than zero, cannot be known precisely. In the light of that, Hertz' contact equation was modified by the addition of an initial starting depth  $h_0$  to improve the goodness of fit. This led to Eq.(30), which was used to fit the elastic loading part of the sx materials and in which a is a proportional constant consisting the tip radius and the reduced modulus of the sample tip contact.

$$P = a \cdot (h + h_0)^{3/2} \tag{30}$$

The load induced shear strain p<sub>m</sub> under the indenter can be calculated with Eq.(31).

$$p_m = \left(\frac{6 \cdot P \cdot E_r^2}{\pi^3 \cdot R^2}\right)^{1/3} \tag{31}$$

This number can be compared to the theoretical shear strength of the material which can be calculated according to Eq. (32). The theoretical shear strengths reported in literature are 115 and 69 GPa for chromium and tantalum, respectively [44].

$$\tau_{th} = \frac{G}{2 \cdot \pi} \tag{32}$$

#### 2.4.7 Pile-ups and Sink-ins

Plastic deformation under the indenter might lead to plastic distortions, either called sink-ins or pile-ups, of the material around it. Both of them are not considered by the Oliver-Pharr procedure [20]. Which one of those actually occurs is expected to be dependent on the ratio of yield strength to Young's modulus and the strain hardening properties of the material. According to [30], materials with a high strain hardening potential (e.g. well annealed or sx metals) might be more likely subject to sink-ins. This is caused by a strength gain of plastically deformed material which leads to a favored flow of the residual material around it. Thus material farther away from the indenter has a bigger share on the overall plastic deformation and the material close to indenter tends to sink in. On the other side materials with low strain hardening potential (e.g. highly deformed metals such as ufg materials produced by SPD) and a high ratio of young's modulus to yield strength are showing a higher susceptibility for pileups. This is for the simple reason that most of the plastic deformation takes place close to the indenter. In Fig. 2.14a a schematic cross-section of an indent shows sink-in behavior on the left side and piling up on the right side. Fig. 2.14b illustrates the actual contact areas of indents which are influenced by a sink-in (left) and a pile up (right) respectively.

#### 2 Theoretical Background

As a result of such distortion the contact area is either underestimated (sink-in) or overestimated (pile-up). Since  $A_c$  is influencing all further analysis results, unnoticed sink-ins or pile-ups might falsify the final experimental results considerably. For indents with a sufficient size, strong distortions are potentially detectable with light microscopy. Otherwise the use of a scanning electron microscope (SEM) is feasible, though only the use of an atomic force microscope (AFM) or similar devices delivers sophisticated information about the distortion's exact geometry. In the past several different procedures had been suggested to take these issues into consideration [45, 46]. However, a very simple procedure to correct the influence of pile-ups and sink-ins is to estimate their heights or depths, by means of atomic force microscopy or similar techniques. The ratio of  $h_p$  to  $h_t$  (Fig. 2.14a) can then be used to adjust the contact depth.



Fig. 2.14: A schematic cross-section of an indent with a sinking-in on the left side and a piling-up on the right side (a). Actual contact are of indents which are subject to sink-in (left) and pile-up behavior (right) (b). Adapted from [30].

## **3** Experimental Procedure

## 3.1 Starting Material

The original material for this work were single crystalline chromium and tantalum rods with a diameter of 10 mm, obtained from Mateck GmbH, Jülich, Germany. Their purities are 5N and 4N for chromium and tantalum, respectively. These were cut by means of a diamond wire saw into about 1 mm thick disc-shaped samples. Since sx and ufg samples were required, one sample of each material was kept in the sx state, whereas three others were processed by HPT to achieve an ufg microstructure without any changes in purity. After the surface preparation, each disc was finally cut into four segments to achieve a higher amount of individual samples.

## 3.2 High Pressure Torsion

For the production of the ufg samples out of the sx discs, the HPT facility at the Erich-Schmid-Institut, Leoben, Austria with a maximum load equivalent to 40t was used. To enable the processing of different materials (e.g. single crystals, powders, etc.) and different sample sizes, the upper and the lower plunger are exchangeable. Before mounting the sample in the lower plunger, the dies and the sample were sandblasted. This was done to increase friction in order to avoid slipping between the rotating upper plunger and the samples.

The HPT runs itself were carried out with the maximum available load of 40 t ( $\approx$ 390 kN), which resulted in an approximate pressure of 4.95 GPa. In total 10 revolutions were conducted at a rotational speed of 0.2 min<sup>-1</sup> on each sample. Due to the high strengths of the final ufg material, the abrasion of the plunger dies was considerably high. Therefore, after every second run, the dies of both plungers were reshaped by lathing and again sandblasted. Altogether three chromium and three tantalum discs were processed which all had a thickness between 0.6 and 0.7mm.
# 3.3 Sample Preparation

The preparation of the surface plays a major role for the accessibility of very fine microstructures to methods of electron microscopy such as BSE and EBSD imaging. Moreover the thorough preparation is crucial for the reliability and homogeneity of nanoindentation experiments. The sx as well as the ufg samples were prepared according to Table 5. In detail, for the microstructural investigations the cross-sections for radius-dependent examination were prepared, for the nanoindentations the top surfaces, respectively (Fig. 3.1).

Table 5 : Overview of the preparation methods for sx and ufg chromium and tantalum. Numbers written in brackets represent the graining of the used polishing method.

	methods		chromium		tantalum
•	mechanical grinding		SiC 500-4000		SiC 800-4000
•	mechanical polishing	-	MD-Dur (9 µm)	-	MD-Largo (9 µm)
		-	MD-Dac (3 μm)	-	MD-Dac (1 μm)
		-	MD-Nap (1 µm)	-	MD-Chem (0.04 μm)
		-	MD-Chem (0.04 μm)		
•	electrolytic polishing	-	electrolyte: A2 (Struers)		-
		-	voltage: 20 V		
		-	time: 10 s		
•	Vibro		-		MD-Nup (0.04 μm)



Fig. 3.1: Illustration of the HPT processed disc (a), a halved disc showing the cross-section (dashed area) where microhardness measurements were conducted (b), and the final sample shape for nanoindentation (grey area) (c).

# 3.4 Microhardness Measurements

Microhardness measurements were conducted on halved HPT-samples (ufg) (Fig. 3.1b) over the whole radial range of their cross-sections for both materials. This was done to obtain the radius dependency of the hardness and hence the onset of the HPT grain size limit. The middle of the cross-sections was used as a starting point, measurements with a spacing of 0.5 mm along the radius of the specimen were subsequently performed resulting in about 21 indents per sample.

The measurements were conducted on a BUEHLER MicroMet 5100. The used loads were 500g (HV 0.5) for chromium and 1000g (HV 1) for tantalum, respectively.

# 3.5 Microstructural Investigations

In order to gain detailed information about the evolved microstructure of the HPT samples, EBSD and BSE imaging was used. This is of major interested because the grain structure exceptionally contributes to the mechanical properties of the material as discussed in chapter 2.1.1. The used SEM was a LEO Gemini 1525 equipped with BSE and EBSD detectors.

As for all techniques based on backscattered electrons, EBSD and BSE signals increase with the atomic number (Z) of the material [47]. Since for the EBSD pattern only the part of electrons satisfying Bragg's law are contributing, this method is particularly delicate to a lack of backscattered electrons. Due to the higher atomic number of tantalum ( $Z_{tantalum} = 73$ ) compared to chromium ( $Z_{chromium} = 24$ ) it was expected to obtain higher quality EBSD maps from tantalum. For this reason the microstructural investigation of chromium was eventually carried out by means of BSE imaging. Since this technique does not allow for an automatized determination of the average grain size, a manual grid method was used. Thereby a grid is superimposed to a BSE image and the number of grain boundaries on a grid line are counted, enabling the calculation of the average grain size. For the EBSD analysis a minimum grain size of ten pixels and a minimum misorientation of 15° where set. For both materials different radial distances from the center of the cross-section were chosen to investigate the dependency of the microstructure and especially the average grain size with respect to the radial position of the sample. In Table 6 the exact positions of the microstructure measurements are shown.

Table 6 : Radial positions of the microstructural investigations of chromium and tantalum					
chromium ufg (BSE) [mm]	tantalum ufg (EBSD) [mm]				
0.0 - 1.0 - 2.0 - 3.0 - 4.0	0.0 - 0.5 - 1.0 - 1.5 - 2.0 - 0.5 - 0.0 - 0.0 - 0.5 - 0.0 - 0.5 - 0.0 - 0.5 - 0.0 - 0.5 - 0.0 - 0.5 - 0.0 - 0.5 - 0.0				
	2.5 - 3.0 - 3.5 - 4.0 - 4.5				

# 3.6 Annealing Experiments

Since the nanoindentation tests were performed at several different elevated temperatures, the chance of a recrystallization of the ufg microstructures had to be investigated prior. The widely known Tammann's law [48] suggests that for highly deformed pure metals, the recrystallization temperature is at about 40% of the melting temperature. Although this is only a very rough estimation (not including the exact degree of deformation, impurities, alloy elements, etc.), it shows the importance of the melting point for recrystallization. Though both materials used in this work are refractory metals which are well known for their high melting points, chromium ( $T_{m, chromium} = 1900^{\circ}$ C) and tantalum are still ( $T_{m, tantalum} = 2996^{\circ}$ C) far apart. Therefore, only chromium was subject to the performed vacuum annealing tests.

The annealing runs were carried out from 100 to 500°C with 100°C steps in between in a XERION vacuum furnace. The temperature profile was set accordingly to a heating rate of 10 °C/min and a dwell time of 60 min. After each annealing the microstructure of the chromium sample was investigated by electron microscopy (BSE) at radial positons of 4mm to the center of the sample.

## 3.7 Nanoindentation

In order to obtain mechanical properties such as hardness, Young's modulus, SRS and activation volume, nanoindentation experiments were conducted. In the following chapter the instrumental setup, as well as the different tests and corresponding parameters are explained. The data processing and plotting was carried out with the manufacturer's software NanoTest Platform Three <sup>®</sup>, Microsoft Excel<sup>®</sup>, and largely using self-written MATLAB<sup>®</sup> scripts.

#### 3.7.1 Experimental Setup

The used nanoindentation facility Micro Materials NanoTest Platform3, Micromaterials, UK (Fig. 3.2a) was located at the Department of Nuclear Engineering, University of California, Berkeley. The setup consisted of the nanoindenter, the vibration damping table it was placed on, and the chamber it was housed in. The latter is required to enable the implementation of the purging gas system. This is thought to keep an extremely low oxygen content atmosphere in the chamber to avoid oxidation and similar undesired influences. For high temperature experiments the nanoindenter was equipped with a high temperature option with heated indenter tip and sample configuration (Fig. 3.2b). This allows a separate controlling of indenter and sample temperature. Because of their high reactivity with transition metals such as chromium and tantalum, respectively, diamond indenters are fairly sensitive to high

#### **3** Experimental Procedure

temperature contact with this type of metals [49]. However, since the maximum temperature for the experiments carried out in this work was only around 300 °C, a diamond indenter ( $E_{diamond} = 72$  GPa,  $v_{diamond} = 0.07$ ) was used for room temperature, as well as for elevated temperature indentation experiments.



Fig. 3.2: Overview of the nanoindenter in the chamber (a). Details of the actual indenting high temperature set-up (b) showing heat shield (1), indenter (2), stage (3), high temperature sample holder and heating system (4) wiring for the sample heater's power supply and the thermocouple (5)

### 3.7.2 Preparation for Nanoindentation

For the room temperature experiments, the samples where fixed to a shaft-shaped aluminum sample holder with super glue. For elevated temperatures a heatable sample holder was used instead (Fig. 3.3). Furthermore high temperature cement (Omega Bond 600) was applied instead of the glue to avoid degradation issues. On the surface of the heated area of the sample holder, the actual specimen and a dummy sample with an attached thermocouple were mounted. While the specimen surface was kept free, the thermocouple was fixed to the surface of the dummy sample with cement. In order to guarantee consistent drying of the wet deployed cement, a waiting time of approximately one day was observed. After attaching the sample holder onto the nanoindenter stage, another hour with the door closed was waited for thermal equilibration.



Fig. 3.3: Dummy sample for temperature controle (1) and indentation sample (2) on the heatable sample holder ("hot stage") (3) with the according wires for power supply and the thermocouple (4).

#### 3.7.3 Experimental Parameters

Though microhardness measurements and microstructural investigations show a fairly wide radial range with similar sample properties for the ufg specimens, a radius of 3.5mm to the former disks center was chosen as testing area. For the single crystalline samples no such limitations were applied. The required maximum loads for each material were determined by test indents. The loading time was chosen to provide a comparable strain rate, whereas the unloading time was set empirically. Though it needs to be mentioned that this leads to different loading and unloading strains. The used set-up provides an automatic drift correction measurement at the end of the (last) unloading curve. This can be seen in Fig. 3.4 and Fig. 3.5.

Basically two different types of experiments were conducted. The first one was to obtain hardness and Young's modulus with short dwell times to avoid distortion caused by creep or thermal drift. These were carried out with a cyclic loading scheme consisting of eight peak loads and thus eight unloading curves such as shown in Fig. 3.4. A further use of these tests was to observe pop-in events on the sx samples. An overview of the parameters for these experiments can be seen in Table (7). The different peak loads for this kind of tests were calculated with Eq. (13).



Fig. 3.4: Load – time schedule used for the cyclic test runs. On the left-hand side an overview is illustrated. The right-hand side is showing the load, dwell and unloading time as well as different loads for one segment of the schedule in detail.

Load Controlled Experiment	load-profile (I) [mN]		load-profile (II) [mN]	loading time [s]	unlading time [s]	dwell [s]
	-	8.85		15	5	
	-	13.25	х			
	-	19.85				5
Chromium ufa	-	29.65				
Chronnum uig	-	44.45				
	-	66.75				
	-	100.00				
	-	150.00				
	-	1.41				
	-	2.11		15	5	5
	-	3.16				
Chromium cy	-	4.74	Ň			
Chromium sx	-	7.11	Х			
	-	10.66				
	-	16.00				
	-	24.00				

#### Table 7 :Load-time schedules for the cyclic indentation runs for all used materials

#### **3** Experimental Procedure

	-	7.00	-	14.63			
	-	10.50	-	21.85			
	-	15.80	-	32.92	15		
Tentelum ufa	-	23.70	-	49.38		F	-
Tantalum utg	-	35.60	-	74.07		5	Э
	-	53.30	-	111.11			
	-	80.00	-	166.67			
	-	120.00	-	250.00			
	-	1.17	-	1.31			
	-	1.76	-	2.35			
	-	2.63	-	4.23			
Tautalum au	-	3.95	-	7.62	4 5	-	-
Tantalum SX	-	5.93	-	13.72	15	5	Э
	-	8.89	-	24.69			
	-	13.33	-	44.44			
	-	20.00	-	80.00			

The second type of experiments was focused on the determination of SRS and V\*. Owing that, a long dwell time at peak load should guarantee a sufficient creep depth. A schematic load-time schedule for these tests is shown in Fig. 3.5. The used parameters can be found in Table 8.



Fig. 3.5: Load – time schedule used for the long dwell time runs.

Load Controlled Experiment	max. load (I) [mN]		max. load (II) [mN]		loading time [s]	unlading time [s]	dwell [s]
Chromium ufg	-	100		х	15	5	200
Chromium sx	-	24		х	15	5	200
Tantalum ufg	-	80	-	120	15	5	200
Tantalum sx	-	20	-	80	15	5	200

Table 8 : Load-time schedules for the long dwell time runs for all used materials.

The temperatures at which the experiments were carried out were slightly different for chromium and tantalum due to their different  $T_c$  values. The chromium samples were measured at 25 °C, 100 °C, 200 °C and 300 °C, while tantalum was measured at 25 °C, 100 °C, 250 °C, and 300 °C.

# 3.8 **Post experimental Investigations**

#### 3.8.1 Pile-ups

Images made of the indents by light and electron microscopy revealed a piling up of material around the indents. This leads to an underestimation of the contact depth and thus distorts the results from nanoindentation (chapter 2.4.7). The AFM-mode of the nanoindenter was used to determine the shape and height of these pile-ups to enable a suitable correction. 200nm was chosen as a step width for the surface scanning process. Afterwards, the data were analyzed and plotted with a MATLAB script.

#### 3.8.2 Indent Cross-Sections

To verify a possible change of the microstructure due to grain growth at elevated temperatures and/or the plastic deformation caused by indentation, cross-sections of the 300 °C indentation runs on ufg chromium and tantalum were made using a focused ion beam. These cross-sections also provide reliable information about the potential formation of an oxide layer on the surface of the material. In order to receive a distinctive and clean surface, a platinum deposition was applied on top of the indent before the milling step.

# 4 Results

# 4.1 Microhardness Measurements

The ufg samples were tested such as described in chapter 3.4. The chromium specimen shows a hardness minimum of 289 HV 0.5 at the center. Measurements at a radial position of 1mm already show hardness numbers of about 500 HV 0.5. After this steep increase, the further curve's slope is flatter, reaching maximum values of about 550 HV 0.5 (Fig. 4.1a). This is about 13% higher than Edalati et al. [50] report for their 200 nm average grain size microstructure. The tantalum sample on the other hand does not show a hardness minimum towards the center, but instead a very evenly distributed microhardness of about 420 HV 1 with a peak value of 438 HV 1 (Fig. 4.1b). In Table 3 (chapter 2.2.2) several reasons for the disappearance of characteristic minimums are discussed. The average hardness of the tantalum is approximately 5% higher compared to literature values [50] which minors the probability of unsufficient strain insertion. Thus, the missing minimum is strongly believed to be caused by an off-centered cut of the sample.



Fig. 4.1: Microhardness versus radial position of the measurements for ufg chromium (a) and tantalum (b).

# 4.2 Microstructural Investigations

To provide sophisticated information about the evolved microstructure of the HPT processed samples, BSE investigations were performed on a chromium and EBSD investigations on a tantalum sample. As described in chapter 3.5, the BSE data were manually analyzed with a grid method, whereas the EBSD imaging allowed for an automated calculation of the grain size distribution.

The chromium sample shows an ufg microstructure (Fig. 4.4a–e) with a peak average grain size of 263 nm ( $\pm$  32 nm) which steadily decreases towards the edge, finally revealing a minimum of 120 nm ( $\pm$  10 nm). This trend can be seen in Fig. 4.2a. The standard deviations for the different radii where calculated using three varying spots of one according BSE image. The evaluated smallest grain sizes are significantly lower than the 200 nm reported by Lee et al. [51], but close to the results of Provenzano et al. [52] which determined about 100 nm.

Tantalum reveals, consistent to the results of the microhardness testing, only a slight dependence of the average grain size to the radial position (Fig. 4.3a-f). Especially at the center, the EBSD image shows a certain elongation of the grains. However, this is believed to be the result of drift influence, rather than the actual microstructure The grain sizes at the center, approximately 100 - 110 nm, are decreasing towards the edge of the sample where they are close to 90 nm. Since the deviations where automatically calculated from one entire EBSD image per radial position, it needs to be interpreted as the grain size distribution of this image, rather than the deviation of different average grain sizes at a certain radial position. An overview of this behavior can be seen in Fig. 4.2b, where the deviation bars are a fifths of the actual grain size. Compared to Edalati et al. [50] and Wei et al [53] reporting 180 nm and 40 nm, respectively, the average grain size numbers are situated right in between, showing not only the influence of different production parameters, but primarily the difficulty of gaining reliable numbers at these small length scales.



Fig. 4.2: Graph showing the average grain sizes and corresponding deviations at different radial positions for Chromium (a) and Tantalum (b).



Fig. 4.3: Overview of tantalum ufg microstructures determined by EBSD at 0.0mm (a), 1.0mm (b), 2.0mm (c), 3.0mm (d), 4.0mm (e) and 4.5mm (f).



Fig. 4.4: Overview of chromium ufg microstructures determined by BSE imaging at 0.0 mm (a), 1.0 mm (b), 2.0 mm (c), 3.0 mm (d) and 4.0 mm (e).

# 4.3 Annealing Experiments

In order to determine a possible grain growth during nanoindentation experiments at elevated temperatures, annealing runs on a chromium ufg sample where carried out. An overview of the results can be found in Fig. 4.5. The average grain size determined as comparison number without any annealing steps was 117 nm  $\pm$  23 nm, see Fig. 4.6a, which is in good accordance to the numbers gained at 4 mm in chapter 4.2. After a slight increase up to 140 nm at 100 °C is measured, the average grain size stays nearly constant till the 400 °C annealing step, at which it is increasing up to 167 nm  $\pm$  32 nm. Finally, after annealing at 500 °C the average grain size was determined to 243 nm  $\pm$  15 nm. The sample was subsequently polished and its microstructure evaluated again, now showing a significantly higher number of 373 nm  $\pm$  49 nm as shown in Fig. 4.6b.

The grain sizes up to an annealing temperature of 300 °C are assumed to be constant, due to the minor changes in between. Actual grain growth probably took first place at the 400 and 500 °C annealing steps, which is hard to determine, since the evaluation for the 400 °C grain size was only done on a BSE image with a non-polished surface. In the light of this issue a grain growth at lower temperatures, especially 300 °C is still improbable, but cannot be precluded. Consequently, for nanoindentation experiments performed at 300 °C on chromium is a possibility required to take into account when rationalizing the data.



Fig. 4.5: Average grain sizes of a chromium ufg sample after annealing runs at different temperatures.



Fig. 4.6: Comparison of the non-annealed reference microstructure with contaminated surface (a) and the annealed at 500 °C and subsequently re-polished one (b).

# 4.4 Nanoindentation

The nanoindentation tests were carried out according to chapter 3.7. For each material and temperature several indents were made with the cyclic loading scheme to evaluate hardness and Young's modulus. With the 200 s dwell time scheme creep data were generated in order to access time dependent properties such as strain rate sensitivity and activation volume. To accommodate for the high number of indents and for the sake of clarity, in the following chapter especially representative and averaged numbers including standard deviations are presented. In general the post indentation drift correction was applied for experiments at elevated temperature, but not for those at ambient temperature. In some cases issues occurred with this type of drift correction, most notably inconsistent drift measurements and excessive correction values. If one indent out of the schedule was predominantly affected by obvious errors caused by the drift correction, it was precluded for the further calculations.

All the indents were made with a minimum lateral distance of 30  $\mu$ m among each other to guarantee that plastic deformation introduced by indentation does not influence the measurements of subsequent indents. Fig. 4.7a and b show the load depth response of the material to the different loading schedules for a tantalum ufg sample at room temperature consisting of six indents each. Fig. 4.7c and show the corresponding light microscopy images of these indents.



Fig. 4.7: Materials response of ufg tantalum at room temperature to a cyclic (a) and to a 200 s loading scheme (b). Corresponding light microscopy images of the indents (c,d).

#### 4.4.1 Hardness and Young's modulus

In this chapter the hardness for different depths at several temperatures are shown next to similar plots for the Young's modulus. Unless otherwise stated, the results are observed from loading profiles denoted as "(I)", see Table 7 and Table 8. At least three indents per temperature were used to calculate the average and standard deviation values. The focus of this chapter is to present and compare the gained results with accessible literature and microhardness testing data. A critical review and an in-depth discussion about possible measurement errors will be done in a subsequent chapter.

Optical and electron microscopy investigations carried out afterward revealed pile-ups which influence the contact depth and therefore all descending numbers as discussed in chapter 2.4.7. The pile-ups have been measured and corrected by increasing all contact depths by 10%, according to chapter 4.4.5.

#### Chromium ultra-fine grained

The hardness of ultra-fine grained chromium is steadily decreasing with increasing temperature, as it can be seen in Fig. 4.8a. While the room temperature as well as the 300 °C hardness curves are straight to a certain degree, the 100 and 200 °C do show a considerable slope. The average numbers are ranging from 5.69  $\pm$  0.09 GPa at room temperature to 4.89  $\pm$  0.24 GPa at 100 °C, to 4.35  $\pm$  0.30 GPa at 200 °C and to 3.76  $\pm$  0.21 GPa at 300 °C. The room temperature number is close to the 5.4 GPa observed by microhardness testing.



Fig. 4.8: Hardness and Young's modulus of ultra-fine grained chromium for different depths at 25, 100, 200 and 300 °C.

The Young's modulus shows, with exception of 300 °C indentations, a decrease when the temperature is elevated as it is shown in Fig. 4.8b. The 100 and 200 °C curves show a significant slope compared to their room temperature and 300 °C counterparts. The averaged numbers range from 295  $\pm$  9.8 GPa to 258  $\pm$  18 GPa to 214  $\pm$  37 GPa to 297  $\pm$  26 GPa for room temperature, 100, 200, and 300 °C respectively. A literature value comparison [44] provides a room temperature Young's modulus of 279.1 GPa, giving a mismatch of less than 6%. The strong decreases of the Young's modulus numbers with increasing depth and therefore higher loads is believed to be caused by a general stiffness problem of the sample to sample holder fixation and not be an intrinsic property of the material. Since the stiffness is contributing to the evaluation of the contact depth as well, the s slopes for the 100 and 200 °C hardness curves might be induced by this stiffness issue. The data of the 300 °C curve were calculated using a comparably high frame compliance, which was evaluated before. It is believed that an overestimation of the frame compliance led to the high Young's moduli at 300 °C.

#### Chromium single crystalline

In general, the hardness numbers of the single crystalline chromium only show a very low increase at lower depths, see Fig. 4.9a, compared to literature data for other bcc materials. The results range between  $1.64 \pm 0.08$  and  $1.55 \pm 0.05$  GPa at room temperature,  $1.42 \pm 0.06$ 

and  $1.21 \pm 0.04$  GPa at 100 °C,  $1.12 \pm 0.05$  and  $0.87 \pm 0.04$  GPa at 200 °C and  $0.88 \pm 0.04$  and 0.79  $\pm 0.03$  GPa at 300 °C. This apparent lack of indentation size effect is completely unexpected and presumably results from experimental issues as will be discussed later.



Fig. 4.9: Hardness and Young's modulus of single crystalline chromium for different depths at 25, 100, 200 and 300 °C.

The Young's modulus results, shown in Fig. 4.9b own, compared to all other materials investigated, higher standard deviations. This is especially true for the 300 °C values which are conspicuously high, similar to the numbers of the ultra-fine grained chromium at this temperature. All curves show decreased values of Young's modulus at lower depths, beneath 300 nm, in comparison to numbers evaluated deeper in the material. The values averaged over all depths are 269 ± 39 GPa at room temperature, 263 ± 39 GPa at 100 °C, 263 ± 49 GPa at 200 °C and 299 ± 114 GPa. The room temperature average is thus only less than 4% lower than reported in literature [44].

#### Tantalum ultra-fine grained

The slopes of the hardness curves steadily increase from room to the maximum temperature of 300°C as shown in Fig. 4.10a. This behavior is so distinctive that at low depths, the hardness at 300 °C reaches the one measured at room temperature. In sum the hardness numbers range from 4.28  $\pm$  0.12 GPa to 4.10  $\pm$  0.03 GPa at room temperature, from 4.21  $\pm$  0.08 GPa to 3.74  $\pm$  0.06 GPa at 100 °C, from 3.59  $\pm$  0.12 GPa to 2.90  $\pm$  0.12 GPa at 250 °C and from 4.39  $\pm$  0.11 GPa to 2.85  $\pm$  0.05 GPa at 300 °C. The 300 °C measurements have been carried out with loading profile (II) in order to reach higher maximum depths. It is remarkable that, though it shows similar hardness values as observed from room temperature measurements at low depths, the lowest values at approximately 1750 nm, come below those measured at 250 °C on, is unexpected and demands and in-depth discussion in order to find a sophisticated explanation. This will be attempted in chapter 5.1.1.



Fig. 4.10: Hardness and Young's modulus of ultra-fine grained tantalum for different depths at 25, 100, 250 and 300 °C. The 300 °C results are observed from indents made with load profile (II).

The Young's modulus, see Fig. 4.10b, is continuously decreasing from room temperature to 300 °C, whereby the 250 and 300 °C moduli are very close. Furthermore, the 100 and 300 °C curves are decreasing with raising contact depth. The averaged values are  $181 \pm 5.6$  GPa at room temperature,  $170 \pm 8.9$  GPa at 100 °C,  $148 \pm 8.3$  GPa at 250 °C and  $141 \pm 13$  GPa at 300 °C. Literature [44] quotes the room temperature Young's modulus of tantalum as 185.7 GPa, leading to a mismatch of less than 3% compared to results presented in this work.



#### Tantalum single crystalline

Fig. 4.11: Hardness and Young's modulus of single crystalline tantalum for different depths at 25, 100, 250 and 300 °C. The 250 and 300 °C results are observed from indents made with load profile (II).

The hardness curves of the single crystalline tantalum, see Fig. 4.11a, all show higher values at lower depths and the other way round. This trend is obviously increasing with temperature. The 250 and 300 °C measurements have been conducted with loading profile (II). This provides

higher indentation depths leading to a similar behavior as observed from the ufg tantalum. The hardness of the room temperature curves range from  $1.49 \pm 0.04$  GPa to  $1.12 \pm 0.01$  GPa at room temperature, from  $0.93 \pm 0.02$  GPa to  $0.71 \pm 0.02$  GPa at 100 °C, from  $2.46 \pm 0.32$  GPa to  $0.70 \pm 0.02$  GPa at 250 °C and from  $2.89 \pm 0.06$  GPa to  $0.89 \pm 0.03$  GPa at 300 °C. Summarized, the hardness at low depths is decreasing from room temperature to 100 °C and is subsequently, at 250 and 300 °C, strongly increasing. On the other hand, at high indentation depths the hardness of the 250 and 300 °C curves are in the same range as those measured at room temperature and 100 °C. Whereby the slopes of the former suggest, that at even higher depths, the hardness might further decrease beneath the room temperature and 100 °C values.

The standard deviations of the Young's modulus numbers are in general higher compared to those observed from ufg samples as presented in Fig. 4.11b. Though the room temperature numbers are higher than those at elevated temperatures, the dependence is not absolutely clear, since the 100 °C measurements reveal lower numbers compared to ones made at 250 and 300 °C. Furthermore, the values at low depths seem to be underestimated just as for the single crystalline chromium. Moreover, the room temperature and 250 °C curves have an increasing trend from approximately 500 nm. This behavior will be discussed in chapter 5.1.1. The averaged Young's moduli are 168 ± 17GPa at room temperature, 144 ± 13GPa at 100 °C, 157 ± 25GPa at 250 °C and 151 ± 18GPa at 300 °C. The Young's modulus measured at ambient temperature has a mismatch compared to literature values [44] of approximately 10 %.

#### 4.4.2 Strain Rate Sensitivity and Activation Volume

The strain rate sensitivity was obtained from creep data measured with 200 s dwell time load profiles as shown in chapter 3.7.3. For each material and temperature, at least three indents were made. The results are shown on one hand as continuous SRS versus strain plots for representative creep curves. On the other hand the average m-values of stage A for all indents at the corresponding temperature were calculated as well. This attempt was chosen to take the fact into account that in a double logarithmic stress versus strain rate plots, the evaluated creep curves do not have a constant slope. This is for example shown in Fig. 4.12. Since each point has a certain hardness and slope in this plot, the SRS is a function of hardness and therefore stress as well. Furthermore it can be easily seen that with the progression of creep, the strain rate is decreasing over several magnitudes, reaching numbers in the range of potential thermal drift. To address this possible problem, the stage A numbers, which are gained at higher creep rates and are hence less sensitive to thermal drift, are evaluated and presented next to the continuous plots as well. Anyway, a discussion about the contribution of thermal drift to the evaluated results is given in chapter 5.1.2.



Fig. 4.12: Double logarithmic plot of hardness versus strain rate for an ufg chromium sample at different temperatures. The varying slopes of the curves reveal that the SRS is a function of the stress

The activation volume is basically calculated from SRS, hardness and temperature. Hence the thermal drift concerns are similar to those discussed above. It furthermore needs to be mentioned, that the lowest values for each SRS curve are observed at the beginning of the creep process at high flow stresses, whereas it is the opposite for V\*. Since the SRS and V\* are strongly related to each other, the according results are presented next to each other.

#### Chromium ultra-fine grained

Experiments conducted at ambient temperature led to continuous SRS curves extending from 0.006 to 0.018. With rising temperature, the SRS of the ufg chromium also increases ranging from 0.025 to 0.197 at 300 °C, as shown in Fig. 4.13a. The 200 °C and 300 °C SRS curves are rather close. The results gained from stage A are similar and shown in Fig. 4.13b. The SRS is rising from  $0.012 \pm 0.002$  at room temperature to  $0.070 \pm 0.007$  at 300 °C. The numbers gained at ambient temperature are in good accordance to data and model-predicted values obtained from yield tests by Wu et al. [19], who reported 0.012 for a 58 nm average grain size sample.

V\* curves obtained at 100, 200 and 300 °C do have a similar trend as those for the SRS as it is shown in Fig. 4.13c. The numbers are ranging from 14 to 40 b<sup>3</sup> at room temperature and 4.3 to 24 b<sup>3</sup> at 300°C, though the lowest numbers are reached with 3.0 to 16 b<sup>3</sup>at 200 °C. The evaluation of the stage A data, see Fig. 4.13d, delivers the highest numbers,  $21 \pm 3$  b<sup>3</sup> at room temperature as well. This is followed by a nearly constant plateau showing 9.9 ± 2 b<sup>3</sup> at 300 °C.



Fig. 4.13: Continuous SRS vs. stress (a), stage A SRS vs. stress (b), continuous V<sup>\*</sup> vs. stress (c), stage A V<sup>\*</sup> vs. stress (d) plots for ufg chromium at different temperatures.

#### Chromium single crystalline

The continuous SRS curves of sx chromium at room temperature range from 0.016 to 0.060. This is initially followed by decreased values at 100 °C of 0.008 to 0.036. This reduction is expected, since bcc single crystals become less rate sensitive towards their critical temperatures. The shape of the 100 °C curve is noticeably different. The slope is steeper, which proposes a faster increasing SRS with respect to stress compared to its counterparts at other temperatures. At 200 and 300 °C the SRS curves are rather similarly shaped compared to the room temperature curve again. This comes in hand with a further SRS elevation. An overview of this results is presented in Fig. 4.14a. Numbers observed from stage A, see Fig. 4.14b, do have the same trend as those observed from the continuous evaluation, reaching from 0.048  $\pm$  0.004 at room temperature, to 0.015  $\pm$  0.002 at 100 °C to eventually 0.049  $\pm$  0.009 at 300 °C. The approximately 0.05 measured at ambient temperature are higher than via yield test determined m of 0.02 reported by Wu et al. [19]. However, this might be caused by the different testing techniques.

The results for the activation volume do follow an according trend as shown in Fig. 4.14c. The V<sup>\*</sup> curve situated lowest is the one representing room temperature spanning between 17 and 52 b<sup>3</sup>. After an increase to numbers measured at 100 °C, ranging from 40 to 172 b<sup>3</sup>, the V<sup>\*</sup> curves of the 200 and 300 °C measurements are decreased again, extending from 27 to 148 b<sup>3</sup> and 34 to 212 b<sup>3</sup>, respectively. As explained for the SRS plot, the 100 °C curve is divergently shaped, showing a steeper decrease of V<sup>\*</sup> versus flow stress. The corresponding numbers for V<sup>\*</sup> obtained from stage A are plotted in Fig. 4.14d. These are 18 ± 2 b<sup>3</sup> at room temperature, 91 ± 10 b<sup>3</sup> at 100 °C, 58± 7 b<sup>3</sup> at 200 ° and eventually 59 ± 17 b<sup>3</sup> at 300 °C.



Fig. 4.14: Continuous SRS vs. stress (a), stage A SRS vs. stress (b), continuous V<sup>\*</sup> vs. stress (c), stage A V<sup>\*</sup> vs. stress (d) plots for sx chromium at different temperatures.

#### Tantalum ultra-fine grained

The results of the continuous evaluation of the SRS can be found in Fig. 4.15a. The curves extend from 0.005 to 0.015 at room temperature, from 0.010 to 0.186 at 100 °C, from 0.018 to 0.421 at 250 °C and from 0.028 to 0.218 at 300 °C. The numbers for the analysis of stage A can be found in Fig. 4.15b. They are 0.010  $\pm$  0.002, 0.024  $\pm$  0.003, 0.063  $\pm$  0.013 and

0.052 ± 0.014 for room temperature, 100 °C, 250 °C and 300 °C respectively. It is obvious from both figures, that the flow stress of the 300 °C numbers is significantly higher than one would expect. While a declining stress is expected when rising the temperature, it is, especially at the start of the creep curve, higher than those measured at lower temperatures. At the end of the creep curve and thus at higher indentation depths, the slope is decreasing. This is an indicator for decreasing flow stress with respect to depth as it was already obtained in chapter 4.4.1 for tantalum ufg at 250 °C, but particularly at 300 °C. The ambient temperature SRS numbers are well comparable with the 0.007 measured via yield test on an ECAP sample presented by Wei et al. [6].



Fig. 4.15: Continuous SRS vs. stress (a), stage A SRS vs. stress (b), continuous V<sup>\*</sup> vs. stress (c), stage A V<sup>\*</sup> vs. stress (d) plots for ufg tantalum at different temperatures.

The continuous results for V\* are ranging from 14 to 41 b<sup>3</sup> at room temperature, from 1.8 to 27 b<sup>3</sup> at 100 °C, from 1.5 to 24 b<sup>3</sup> at 250 °C and finally from 2.7 to 14 b<sup>3</sup> at 300 °C and are displayed in Fig. 4.15c. The stage A results, shown in Fig. 4.15d, span from 20 ± 4 at ambient temperature, to  $13 \pm 1$  b<sup>3</sup> at 100 °C, to  $8.1 \pm 2$  b<sup>3</sup> at 250 °C and to  $5.8 \pm 1$  b<sup>3</sup> at 300 °C.

#### Tantalum single crystalline

Different to the other materials in this chapter, creep curves are presented of the 300 °C sample after the high temperature experiments at room temperature with two different load profiles additionally. This is to show the influence of the observed hardening of the tantalum after indentation runs at elevated temperature to the SRS and V\*.



Fig. 4.16: Continuous SRS vs. stress (a), stage A SRS vs. stress (b), continuous V<sup>\*</sup> vs. stress (c), stage A V<sup>\*</sup> vs. stress (d) plots for sx tantalum at different temperatures.

The room temperature SRS numbers range between 0.014 and 0.056. At 100 °C the numbers declined as it was expected and as well the case for the sx chromium. The SRS is spanning from 0.008 to 0.022, whereas the flow stress is lower as well compared to room temperature. The 250 °C curve shows a different behavior. While the flow stress has overall increased and is even higher than those obtained at room temperature, the SRS numbers at the beginning of the creep curve are lower, namely 0.007, compared to the 100 °C curves, but increase to eventually 0.074. The curve measured at 300 °C is situated at even higher flow stresses, but showing the highest SRS values of 0.025 to 0.260. After cooling down the 300 °C sample was subject to two further indentation runs, one with the usual 20 mN load profile – "profile (I)" - and one with

an 80 mN load profile – "profile (II)", leading to pre-creep contact depths of approximately 500 and 1350 nm, respectively. As it can be seen in Fig. 4.16a, the SRS of the pre-heated sample loaded with the 20 mN profile has significantly declined, just extending from 0.008 to 0.021. Furthermore, the flow stress has substantially raised, representing the highest numbers measured on this material. The stage A data, shown in Fig. 4.16b, match this trend. They proceed from the reference room temperature numbers of  $0.042 \pm 0.002$ , to  $0.020 \pm 0.002$  at 100 °C, to  $0.026 \pm 0.005$  at 250 °C and to  $0.067 \pm 0.012$  at 300 °C. The subsequent tests at room temperature revealed SRS values of  $0.021 \pm 0.002$  for load profile (I) and  $0.033 \pm 0.000$  for load profile (II). For both methods of evaluating the SRS, it is standing out that the room temperature results show a relation between the tantalum hardening after high temperature experiments and the measured strain rate sensitivities. The SRS seems to decrease with increased hardening. However, the ambient temperature SRS is in the order of the results of yield tests on coarse grained tantalum published by Wei et al. [6].

All room temperature experiments show rather similar results in terms of activation volume, which is shown in Fig. 4.16c. This is due to the fact that a contrary variation of hardness or stress on the one hand and SRS on the other hand compensate each other when calculating V<sup>\*</sup>. The room temperature reference sample shows V<sup>\*</sup> in the range of 18 to 58 b<sup>3</sup>. The highest values, namely 73 to 178 b<sup>3</sup>, are received from the 100 °C measurement which arise from rather low flow stress and SRS. The 250 °C curve is showing the widest range of V<sup>\*</sup> values, extending from 18 to 160 b<sup>3</sup>. At 300 °C the numbers are spanning between 4.7 and 35 b<sup>3</sup>. The general characteristics hold true for the stage A values, presented in Fig. 4.16d. The V<sup>\*</sup> numbers of the reference room temperature sample is 22 ± 1 b<sup>3</sup>, whereby the further numbers are 75 ± 6 b<sup>3</sup> at 100 °C, 51 ± 9 b<sup>3</sup> at 250 °C and 15 ± 3 b<sup>3</sup> at 300 °C.

#### 4.4.3 Size Effect and Macroscopic Hardness

The hardness and depth data gained from previous experiments, shown in chapter 4.4.1, are the initial data for the analysis of the ISE. The ISE for chromium as well as for the tantalum sx samples was not as distinctive as expected for single crystalline materials. In fact the hardness was, with exception to the tantalum sx tested at elevated temperatures which show a hardening phenomenon, not significantly increasing at lower depths. In Fig. 4.17 Nix-Gao plots for chromium and tantalum are shown. The presented data points are gained from representative room temperature experiments and lead to h<sup>\*</sup> numbers of 27 and 134 nm for chromium and tantalum, respectively. A comparison with other bcc sx materials, see Fig. 2.11, reveals how low these numbers are. They are in the range, especially in terms of the chromium, of what would be expected for an ufg or nc microstructure, rather than for a single crystal. The results at elevated temperature show, besides the mentioned exceptions, the same unexpected low h<sup>\*</sup> numbers, which is the reason why they are not additionally presented. This leads to the assumption that either the measurements itself, or the analysis contain falsifying errors. Since only indentation data are used which show a distinctive pop-in event, which are only observed for sx and coarse grained materials, the possibility of material caused errors is

precluded. A further discussion as well as a comparison with measurements conducted on a different nanoindentation system are presented in chapter 5.1.3.



Fig. 4.17: Nix-Gao plots for sx chromium (a) and for sx tantalum (b) at room temperature.

#### 4.4.4 Pop-Ins

In order to compare the shear stress at the occurrence of a pop-in event  $\tau_{pop-in}$  with the theoretical strength of an idealized crystal  $\tau_{th}$ , the radius of the tip of the Berkovich indenter, which was assumed to be spherical, needed to be evaluated. This was eventually done according to chapter 2.4.6 using reduced moduli calculated with Eq.(23) and literature values for chromium, tantalum and diamond, namely 278 and 186 and 1147 GPa [44], respectively. Since the high temperature experiments are more likely to be influenced by thermal drift and decreased moduli of the material, these were not used for the tip radius evaluation. The high temperature runs might even affect the data gained post-experimentally, which is why the evaluation of the tip radius was done with a special focus on results obtained at room temperature before heating. A representative example for the pop-in behavior and the according fitting of the elastic loading part of an sx chromium sample at room temperature can be found in Fig. 4.18. The resulting tip radius for these loading curves is 533 ± 58 nm.

Even with the mentioned restrictions to the used data, the determined effective tip radii were subject to distinctive fluctuations between 350 and 500 nm. Furthermore a general increase of the tip radii seems to occur at latest after the 200 and 250 °C runs, which might be caused by abrasive reactions between the indenter tip and the material. However, it was also noticed that the calculated tip radius tends to increase with increasing pop-in load, even when the different indents can be assumed to be made with the same tip geometry. The results regarding the materials strength presented in this chapter, were eventually calculated with a tip radius of 450 nm with exception of those made after the 250 °C experiments for which a tip radius of 500 nm was used.



Fig. 4.18: Load versus depth plot of sx chromium at room temperature showing characteristic pop-in behavior (a) and the elastic loading part before the pop-in with the according fitting (b).

Besides the explicit room temperature sample, pop-in experiments were carried out also at ambient temperature before and after the high temperature runs. But not only is the sheer number of indents made lower at elevated temperatures, also the probability of unambiguous pop-in events decreased for both materials with rising temperature. The results of the explicit room temperature sample and all pre-heating room temperature tests are presented together as "RT" in the following charts. While those made after the high temperature experiments are named "RT\*" for the 100 °C sample, "RT\*\*" for the 200 and 250 °C data for tantalum consist on one side of the dedicated 200 and 250 °C target temperature samples and on the other hand of those measured at the mentioned temperatures on the subsequently measured 300 °C samples.

#### Chromium single crystalline

Altogether 101 pop-in events were observed on the four different chromium samples. A general trend is that the overall loads at which they occur is decreasing with rising temperature as shown in Fig. 4.19a. It is also apparent that the variation of the pop-in loads is also most pronounced for those at room temperature. These range from approximately 0.1 up to 2.5 mN, whereas those at elevated temperatures are less scattering. This difference is probably caused by the fact that the room temperature curve is consisting all pop-ins obtained from the dedicated room temperature sample as well as those made on the other samples before heating. The mentioned features are consistent to those in Fig. 4.19b, showing the ratio of  $\tau_{pop-in}$  to  $\tau_{th}$ . The highest and the lowest strength were consequentially observed on the room temperature, being 0.63 at ambient temperature and 0.37 at 300 °C. This equals to a shear strength of approximately 11 GPa which is in very good accordance to the results obtained from coarse

#### 4 Results

grained chromium presented by Wu et al. [42] for a similar tip radius. The diminishing strength at elevated temperatures on the other hand, seems to be an underestimation compared to another work of Wu et al. [54], were they report a reduction of approximately 5% at 200 °C, whereas it is 20% in this work. However, the lower number of pop-ins observed at elevated temperatures is complicating the comparison.

The indentation runs at room temperature after the high temperature tests delivered strength numbers in the range of those observed at room temperature before heating. This is only with the exception to RT\*\*\*, where the average relative shear strength is modestly decreased to 0.47. Moreover, all post high temperature strength numbers are higher than those observed at the corresponding elevated temperatures, which suggests that the reduced strength of the high temperature measurements were temperature caused. If significant annealing of dislocations would have occurred, it would be expected, that the shear strength of the post high temperature tests would be increased which is not observed. However, such a comparison would require better statistics for a more definite statement.



Fig. 4.19: Overview of pop-in events obtained at different temperatures on sx chromium plotted as cumulative probability versus pop-in load (a) and as relative theoretical strength versus temperature (b).

#### Tantalum single crystalline

For the tantalum samples 118 pop-ins were observed at different temperatures. In general, the temperature dependence on the pop-in load, an overview can be found in Fig. 4.20a, is not as simple as for the sx chromium samples discussed above. The pop-in load data gained at room temperature exhibit the most spread, as was observed for the chromium previously. With only a few exceptions, the variation of the 100 and the 300 °C curves are low, compared to the others. The average relative shear strength of the room temperature measurements, which are again spreading the most, is 0.77 as shown in Fig. 4.20b. The same value holds true for 100 °C. After a slight increase to 0.81 at 250 °C it declines to 0.62 at 300 °C. The room temperature and 100 °C numbers equal approximately 8.5 GPa shear strength, which is about

13% higher than what Biener et al report [55] for sx tantalum at ambient temperature. Statistical issues due to the low number of pop-ins observed might be accountable for the increasing trend up to 250 °C instead of a modest decrease which would be expected. This is even a possible explanation for the noticeable low average strength of the 300 °C data, which's range is very similarly to those measured at 250 °C.

In the RT\* experiments, only two pop-ins were obtained. However, their shear strength is in very good accordance to the averaged comparison RT numbers. A different picture is given by the RT\*\* and RT\*\*\* tests, which's shear strengths for certain pop-ins even exceed the theoretical strength of tantalum. The highest calculated shear stress is 11.96 GPa, approximately 9 % over the materials actual limit. This behavior might be caused by different reasons, such as a different tip blunting than assumed for calculation, or an increased thickness of the natural oxide layer on the surface of the tantalum sample.



Fig. 4.20: Overview of pop-in events obtained at different temperatures on sx tantalum plotted as cumulative probability versus pop-in load (a) and as relative theoretical strength versus temperature (b).

Summarized, particularly the low number of pop-ins gained from post- and elevated temperature experiments leads to the need of a critically reflection of the received results. The room temperature strengths of chromium and tantalum are well comparable to those presented by other authors as discussed above, whereas those of the high temperature experiments are more demanding due to statistical thoughts. The fact that all shear strengths calculated from pop-in events display a significant portion of the theoretical strength of respective material leads to the assumption that, as assumed in literature [43, 54, 56], the pop-ins mark the nucleation of dislocations in the material beneath the indenter tip.

In order to gain more detailed information about the nucleation process, weather it is of homogenous or heterogeneous nature, it became well established to use a statistical model developed by Mason et al. [41] estimating the activation volume. However, this last analysis step has yet to be done.

#### 4.4.5 Pile-Ups

In order to take pile-ups into account and correct for their falsifying influence on the contact depth, AFM-mode scans were conducted on two different room temperature indents on each material. The lateral resolution was set to 0.2  $\mu$ m and the scan size was selected to be 12  $\mu$ m by 12  $\mu$ m. Since the indenter tip is used as a probe in this method, the maximum depths to be reached are limited. This leads to seemingly similar indentation depths in the result images, though they are not.



Fig. 4.21: AFM mode scans of ufg chromium (a), sx chromium (b), ufg tantalum (c) and sx tantalum (d).

In Fig. 4.21 for each material one AFM image is shown from a 30° azimuth viewpoint. As it is obvious, the pile-up behavior of the two ufg materials is similar. The indents are surrounded by elliptically shaped elevations which are steadily decreasing to the tips of the triangular indent. The results of the sx materials are also well comparable, although being different from the ufg samples. The elevations are more belly-shaped and reach farther in perpendicular directions of the indents edges. All surfaces show a certain degree of tilting, which influences the pile ups in such a way that, those on the upper side outrun the others in terms of size. This is especially distinctive for the measurements on sx tantalum in Fig. 4.21d which is consistent

#### 4 Results

to the fact that this sample owns the highest tilt angle of 1.9°. These deviations from a perfectly perpendicular contact between the surface and the vertical axis of the indenter tip can be caused by preparation imperfections or the mounting of the sample on the holder.

The resulting 3D images were analyzed and led to an underestimation of the non-pile-up corrected contact depth of approximately 10 %. Considering that only two room temperature indents were scanned, this is an estimation rather than an exact value. The data presented in chapter 4.4.1, 4.4.2 and 4.4.3 were all corrected using this approach.

#### 4.4.6 Indent Cross-Sections

In order to investigate the impact of the plastic deformation to the microstructure of the ufg samples and to investigate whether an oxide layer of a certain thickness was formed during high temperature experiments, cross sections of the indents were made with a focused ion beam (FIB) workstation. As a first step platinum in a rectangular shape was depleted via gas deposition as it can be seen in Fig. 4.22a. This is thought to keep the material to indent transitional area clean and enable the observation of a possible thick oxide layer. In Fig. 4.22b the cut proceeding can be seen in the coarse (high current) setting leading to streaks (vertical lines) in the cross section. A subsequent fine cut step removes the streaks giving a clean cross-sectional surface as shown in Fig. 4.22c. Since the grain size of the investigated ufg samples is close to 100 nm and the detector therefore reaches its limits in terms of resolution, an ion beam etching step on the cross sectional surface was subsequently performed. The etching rate is depending on the orientation of the grains, which is why a certain height profile is formed, giving more contrast due to shading effects. The etching current was 0.3 nA for chromium and 0.1 nA for the tantalum sample.



Fig. 4.22: Workflow of a cross-section cut on a chromium ufg sample showing the indent with the platinum depletion (a), the cross section after the coarse (b) and after the fine cut step (c).

Additionally to the mentioned benefits of a cross-sections investigation, in theory also the previously discussed pile-ups, see chapter 4.4.5, should be observable. In practice, this is only hard to accomplish, since the pile-up heights of the ufg materials are supposed to be in the

range of 100 nm, whereas the SEM images have a size of several micrometers. Owing to this fact, pile-ups in the cross-section images can only be assumed to be noticeable.

All pictures presented in the following chapter are captured with a secondary electron (SE) detector and are besides cropping not post-processed.

#### Chromium ultra-fine grained

The microstructure beneath the analyzed room temperature indent, see Fig. 4.23a, is well comparable with the microstructure obtained from the BSE measurements presented in chapter 3.5. The deposited platinum layer is, though being close to completely white in the image, displaying a well-defined boarder to the cross section surface with no further layer in between. The cross section of a 300 °C indent is shown in Fig. 4.23b. Since both indents were approximately cut centrically and made with the same cyclic schedule with a maximum load of 150 mN, it is consistent that the 300 °C indent is deeper. It is furthermore apparent from comparing the microstructures next to each other, that the grain size of the 300 °C sample is increased compared to its room temperature counterpart. This is in good accordance to the measured hardness of the 300 °C sample, which is the only one which does not regain its full quantity in this respect after the high temperature experiments. Although the annealing tests presented in chapter 4.3 do not fully suggest a grain growth at 300 °C they cannot preclude it either. Moreover, for the mentioned annealing tests a dwell time of only 1 h is comparably low to the approximately 12h the sample was exposed to 300 °C during the nanoindentation tests.

The plastic deformation opposed to the material beneath the indenter leads for both cases to a only short-ranged deformation of the grains close to the indent.



Fig. 4.23: Cross sections on ufg chromium indents conducted at room temperature (a) and at 300 °C (b)

#### Tantalum ultra-fine grained

The ufg microstructure received by the cross section analysis of the room temperature sample, shown in Fig. 4.24a, exhibit again similar characteristics compared to what was obtained from EBSD scans. The same holds true for the 300 °C image, see Fig. 4.24b, which is only smaller due to an off-centered FIB cut. Although much more of the platinum layer is left after cutting and etching on the room temperature sample, it is also evident for the 300 °C sample that no interlayer between the platinum and the sample material, emerging for example from oxide formation, is visible. The deformation of the grains beneath the indents is, as previously for the ufg chromium, of short ranged nature. Moreover it seems at least for the room temperature sample that the grains adjust their orientation to the indent geometry to a certain degree.



Fig. 4.24: Cross sections on ufg tantalum indents conducted at room temperature (a) and at 300 °C (b)

After the analysis of the cross sections some important statements can be made. For none of the heated samples an oxide layer was observable between the platinum deposition and the material beneath the indent. Since the formation of oxides is for thermodynamic reasons preferential at higher temperatures, it is assumed that no such layers have formed for the other elevated temperature samples either.

Whereas the microstructure of the tantalum ufg sample did not change, as far as the limited resolution allows to say, the grain size of the chromium ufg sample apparently increased. Both observations are consistent to post high temperature hardness test on those materials. These revealed a full recovery of the hardness in terms of tantalum, but a certain loss in terms of the chromium ufg sample. Since the 200 °C chromium ufg sample, where no cross section is presented, also showed a full recovery of hardness, it is assumed that neither this nor the 100 °C chromium sample were subject to grain growth.

# 5 Critical Discussion on some Experimental Challenges

# 5.1 Nanoindentation

#### 5.1.1 Hardness and Young's modulus

The previously in chapter 4.4.1 presented hardness and Young's modulus results show some unexpected features. Their potential causes will be discussed in the following chapter.

#### Influence of Temperature on the Young's modulus

Room temperature measurements of the Young's modulus revealed for both materials numbers well matching those cited in literature. Moreover, those obtained from ufg samples do not show a certain depth dependence, whereas those calculated from tests on the sx materials at room temperature show reduced values at lower depths. The latter behavior was also observed at comparison measurements on an in-house nanoindentation system, but its cause still needs to be evaluated. However, the Young's modulus numbers at elevated temperatures partly decrease stronger than what would be expected, according to chapter 2.1.2. This is in most cases strongest pronounced for higher indentation depths and is strongly believed to be a frame stiffness problem arising from the mounting of the sample for high temperature experiments, while it is for high temperature and subsequently conducted room temperature tests. In detail, it is thought that during the heating process the sample loosens which leads to an underestimation of the frame compliance. At high loads and depths, this leads into low numbers of Young's modulus due to the underestimation of the sample stiffness.

#### Influence of the System Stiffness on the Hardness

Above the depth dependence of certain Young's modulus curves is discussed. This is often accompanied by a depth dependence of the hardness as well, which is, due to  $h_s$ , influenced by an underestimation of the frame compliance as well. The retrospective correction of the hardness for a constant Young's modulus is possible, but very effortful since a wrong frame

compliance falsifies the displacement raw data and hence contributes to errors in the analysis. However, an example were it is strongly believed that the underestimation of the sample stiffness leads to reduced numbers of hardness at elevated depths is presented in Fig. 4.8a and b. The 200 °C Young's modulus numbers decrease from approximately 270 to 160 GPa with respect to depth. A similar trend is observable for the according hardness, decreasing from approximately 4.6 to 4.0 GPa. For comparison, the room temperature Young's modulus and hardness numbers, plotted in the same figure, do not show depth dependent behavior. In the light of this comparison, it becomes evident that stiffness issues can cause an artificial depth dependence of the hardness, though it is less distinctive compared to the influence on the Young's modulus.

#### Tantalum hardening at elevated temperatures

On all tantalum samples, sx and ufg, a very pronounced hardening was observed when they were heated up to 250 or 300 °C, respectively. Moreover, the strength of this effect was increasing with the time the sample was kept at mentioned temperatures. Two different explanations appear obvious for which one can assume that a certain amount of oxygen or other atmospherical gasses was present in the housing of the nanoindenter. Although the purging gas system was enabled before starting the high temperature experiments, the used argon gas is limited in its purity and is therefore a potential source of non-inert gases.

The first possibility is the formation of a tantalum oxide layer with a significant thickness on the sample surface. Vermilyea [57] report about oxide growth in 99.5% pure oxygen atmosphere at temperatures up to 300 °C for 278 hours. Although these are more severe conditions compared to those experiments were conducted at in this work, the oxygen growth is only in the several 10 Å range, as shown in Fig. 5.1a. Hardness tests conducted on sx tantalum (Fig. 4.11a) furthermore suggest influence depths of approximately 2000 nm, which is. Oxide layers of according thickness are expected to be clearly visible when investigating the cross-sections of affected intents. This was not the case as it is shown in Fig. 4.24b for an indent made on ufg tantalum at 300 °C. Finally, a considerable change of the Young's modulus would be expected for tantalum oxide. This is also not observed as displayed in Fig. 4.11b.

Different to an oxidation, the possible oxygen presence might also lead to a solid solution hardening of the tantalum. The hardness decline with respect to depth might be an evidence for such a diffusion controlled hardening. In fact, tantalum was used as a reference material in the past to show this mechanism in bcc metals due to its good solubility for nitrogen and oxygen [58]. Furthermore, Schmitz et al. [59] report increased hardness for tantalum coatings exposed to oxygen at 350 and 450 °C, whereas Smialek et al. [60] present data showing a shear stress increase by the factor of four at low strains for an oxygen content of 1040 ppm, see Fig. 5.1b. However, all these works have in common, that the solution of oxygen in tantalum was accompanied by some effort to gain samples with certain amounts of dissolved oxygen. Therefore the partial pressure of non-inherent gases which the samples from this work were exposed to are presumably far lower. To substantiate the possible hardness increase from solid

solution hardening it is required to measure the oxygen concentration on the surface and at elevated depths. For literature discussed above, the hardening effects were observed at oxygen concentrations of several 0.1 at.%. As it is widely known, this is beyond the resolution limits of the energy dispersive x-ray spectroscopy method, requiring more sophisticated techniques, just as secondary ion mass spectrometry, or a chemical analysis. Summarized, the evidence speak in favor of the solid solution hardening, since a simple oxidation seems - due to the investigation of cross-section SEM images - improbable. However, last certainty can only be provided by conducting the mentioned oxygen concentration analysis.



Fig. 5.1: Oxidation behavior of tantalum in 99.5 %  $0_2$  atmosphere (a) and effect of interstitial solid solution hardening for sx tantalum at 177 °C (b) adopted from [57] and [60], respectively.

#### 5.1.2 Strain Rate Sensitivity and Activation Volume

Different to the ISE the SRS and V\* are not strongly dependent on the used area function. This is due to the fact that the creep measurements are started at depths over 500 nm where the area function is not as sensitive to calibration errors anymore. On the other hand, the 200 s creep tests are susceptible for the influence of thermal drift which arises from a non-isothermal contact between the indenter tip and the sample. Though the used system heats both separately and makes use of a contact procedure which is designed to minimize temperature differences, it was obtained that thermal drift occurred and that for some cases the post-indentation drift correction is not reliable. Since the creep rates in the end of the dwell time were for some cases suspiciously high, suggesting a positive thermal drift rate, the system often corrected for negative drift rates and hence increased creep depth and SRS. The drift correction was usually in the range of 0.3 to - 0.1 nm/s. Therefore, some distinctive creep curves are plotted with different artificial drift corrections to show the pronounced influence.

In Fig. 5.2a and b creep data of the 250 °C curve, already presented in Fig. 4.15a, are shown with its counterparts superimposed with different drift rates. These data were chosen since
#### 5 Critical Discussion on some Experimental Challenges

the SRS at the end of the dwell time are suspiciously high. The same holds true for the ufg chromium. The results are similarly shaped curves, but especially different maximum SRS are obtained, just as expected. The curve corrected with -0.3 nm/s is only ranging from approximately 0.02 to 0.1 compared to the original spreading of 0.02 to 0.4. In order to enable a comparison, the original room temperature data are plotted in light gray in Fig. 5.2b additionally. The positive correction seems improbable since the strain rates keep very high even at the end of the dwell time. For example, close to 200 s dwell time, the artificial drift rate is contributing to approximately 50 % of the entire strain rate of the + 0.3 nm/s curve.



Fig. 5.2: Creep data with superimpose drift for ufg tantalum presented as hardness vs. strain rate (a) and SRS vs. stress plot (b).

Another particular example is the sx chromium which showed, just like the sx tantalum, unexpected high SRS numbers at 200 and 300 °C. The original data can be found in Fig. 4.14a, whereas those superimposed with artificial drifts are presented in Fig. 5.3a and b. In order to enable a comparison to the SRS curves measured at lower temperatures, the room temperature and 100 °C curves are plotted next to it in Fig. 5.3a. For the above mentioned reasons, the focus is again on the negative correction. The SRS of bcc single crystals is expected to decrease towards its critical temperature, as it was discussed in previous chapters. This decrease was only obtained for the 100 °C data, not for those above. If a negative correction is applied, the peak SRS is decreased closing up to the region where they would be expected. For example, the original 300 °C data range from 0.013 to 0.102 whereas the -0.3 nm/s correction delivers a spreading from 0.007 to 0.02.



Fig. 5.3: Creep data with superimpose drift for sx chromium presented as hardness vs. strain rate (a) and SRS vs. stress plot (b).

This approach of adding drifts of certain rates to the creep data, altering the SRS, is to assess the range a possible thermal drift might have influenced the creep data and hence the SRS. It is, on the other hand, not able to estimate the value of drift which actually occurred during the experiments.

#### 5.1.3 Indentation Size Effect

In order to evaluate reliable numbers for characteristic parameters of the ISE, the hardness and depth values must be measured accurately, but especially in the lower depth regimes. This is because the fit in the Nix-Gao model is most sensitive to high numbers of the reciprocal contact depth. This is also the regime were the finding of an exact area function for the indenter tip is most demanding and hence often subject to errors. In Fig. 5.4a the relative contact area with respect to depth is plotted for two different area functions, the original one, "AFO" and a modified version of it, "AF1". Fig. 5.4b shows the sx tantalum ISE already presented in chapter 4.4.3 and the according analysis with the modified area function. Compared to the original one, the parameters C2 and C3 were changed (Table 9) in order to show the significant influence of those to the ISE. The results show that while H<sub>0</sub> is decreased by less than 5%, h<sup>\*</sup> is increased by 133% to 313 nm. This is in the range of what would be expected for sx tantalum.

From Fig. 5.4a it is apparent that even at higher depths the contact area calculated with AFO and AF1 do not reach the curve of the idealized geometry, though this would be expected. This can be an evidence for a general overestimation of the contact area and hence an underestimation of the hardness since all area functions used show a similar behavior. Furthermore the area functions suffer from too low values at lower depths, especially beneath 200 nm, which is in particular decreasing the calculated ISE as well. For example, the analysis shown in Fig. 5.4b without the shallowest depth data leads to h<sup>\*</sup> numbers of approximately

200 and 400 nm for AF0 and AF1 respectively. Besides the area function, the material itself is of course a possible cause for the unexpected results regarding the ISE. To be able to preclude the material as an error source, comparison measurements with an in-house nanoindentation system were conducted. The h<sup>\*</sup> numbers calculated from room temperature experiments were approximately 350 and 450 nm for sx chromium and tantalum respectively.

Summarized, the AF is strongly believed to be the major source of the unexpected results in terms of the ISE. This is underlined by the reasonable numbers of h<sup>\*</sup> measured with the inhouse nanoindenter for the same samples.



Fig. 5.4: Relative contact area of AF 1 to AF 0 with respect to depth (a) and the according Nix-Gao plot of sx tantalum at room temperature for both area functions (b).

Table 9 : Overview of differe	nt parameters of area	functions plotted in Fig. 5.4
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	C1	C2	C3
AF 0 (original)	27.63	2026	6360
AF 1 (modified)	27.63	1013	0

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### Hardness and Young's modulus analysis

clear all	
close all	
clc	
% file search	
% =======================	
/0	
% file directory	
p dir = 'D:\Matlab F	iles';
% function file director	y
f_dir = 'D:\Matlab Fi	les\functions';
% data directory	
file_dir = 'D:\Studium'	Diplomarbeit\Nanoindentation\Data\Vergleiche\Dif Temperatures\Ta sxx\HE Experiments\data files';
% export directory	
ex_dir = file_dir;	
% load depth hysteres	s file name
file_name = {'T19 TaSx	x1 IcCyc1-20 6inds cc innr3 dcoff.txt';
'T6 TaSxx2 IcCyc1-20 6	inds T100.txt';
123 TaSxx3 IcCyc1-80	5inds 1250.txt;
127 135XX4 ICCyC1-80	Sinus 1500.txt
Б	
% data selection	
% ===============	
sched = [1]; % o	lata files used from 'file_name'
temps = [1 2 3 5];	% specifies colors and markers for different temperatures
array = [1 2 3 4 5 6];	% indents used
CycStartNr = 0;	% skip indents within nr
s_ise = 1; %	schedule nr. for ISE plot
AF_split = 'on';	% AF corrected used?
AF_used = 'old';	% ISE calculated with original AF> 'old' with new AF> 'new
split = 'on';	
HE_plot = on;	
YM_plot = 'off';	
ise = on;	
info dico = 'on';	
nno_usp = on,	
nr inds max = 6:	
nr cycs max = 8:	
$nr_colums = 12$ :	
% material properties	
% ================	
Edia = 1147;	
ndia = 0.07;	
ny_mat = 0.21;	
% ny chromium = 0.21	
% ny tantalum = 0.34	
% corrections	
% =======	
LUTTH = 0.85;	
COFFE = 0.92;	

corrdc = 1.10;
AF_old = [25.09 2180 9173]; AF_new = [27.63 2026 6360];
% plotting properties %
% axis limits Hmax = 5.0; Y_ise_max = 2.5; % set = 0 to activate auto mode Emax = 400; Xim = [0 1200]; dcmin = 100;
s_spec = {'25°C'; '100°C'; '250°C'; '300°C'; '25°C after'};
% legend postion leg_pos = 2; leg_pos_list = {'NorthWest'; 'NorthEast'; 'SouthWest'; 'SouthEast'};
<pre>cm1 = [0.9 0.1 0.1]; % dark red cm2 = [0.1 0.1 0.9]; % dark blue cm3 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.7 0.0]; % Temp color map cmk = zeros(4,3); % black cms = [0.0 0.1 0.9; %RT 0.7 0.1 0.0; %100°C 1.0 0.3 0.0; %200°C 1.0 0.3 0.0; %200°C</pre>
1.0 0.5 0.0; %250°C 1.0 0.7 0.0; %300°C 0.0 0.1 0.9]; % special settings
ms = { v'; 'd'; 's'; 'o'; '<; '^'};
<pre>mz_p1 = 8; % marker size plot 1 mz_p2 = 5; % marker size plot 2 mlw_p1 = 2.0; % marker line width plot 1 mlw_p2 = 2.0; % marker line width plot 2 llw_p1 = 1.5; % line line width plot 1 llw_p2 = 1.5; % line line width plot 2</pre>
FontSize1 = 14; % lable font size FontSize2 = 14; % tick number font size
<pre>font_n = 'Calibri'; % font name</pre>
eb_width = 80; % error bar width in 'units'
scale_dc = [1 100 150 300 500 1000]; % ticks for second x-axis of ISE plot
AxCorr = Hmax/Emax;       % correction for 2nd y-axis         std_os = 1;       % error bar oversizing
% loading data %
cd(file_dir);
N = length(sched);
M = zeros(nr_inds_max*nr_cycs_max, nr_colums, N);
for i = 1:N
<pre>file_ID = fopen(file_name{sched(i)}); C = textscan(file_ID, '%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f</pre>
end
cd(f_dir);
% arrange values %
% defining variables nr_inds = zeros(N,1); nr_cycs = zeros(N,1);
dcl = zeros(nr_cycs_max, nr_inds_max, N); Pl = zeros(nr_cycs_max, nr_inds_max, N); Hl = zeros(nr_cycs_max, nr_inds_max, N);

rml = zeros(nr\_cycs\_max, nr\_inds\_max, N); El = zeros(nr\_cycs\_max, nr\_inds\_max, N); Hr = zeros(nr cycs max, nr inds max, N);

Er = zeros(nr\_cycs\_max, nr\_inds\_max, N); dcr = zeros(nr\_cycs\_max, nr\_inds\_max, N);

Hav = zeros(nr\_cycs\_max - CycStartNr, N); Hav\_new = zeros(nr\_cycs\_max - CycStartNr, N); Eav = zeros(nr\_cycs\_max - CycStartNr, N); dcav = zeros(nr\_cycs\_max - CycStartNr, N);

stdH = zeros(nr\_cycs\_max - CycStartNr, N); stdr = zeros(m\_cycs\_max - CycStartNr, N); stdE = zeros(nr\_cycs\_max - CycStartNr, N); stddc = zeros(nr\_cycs\_max - CycStartNr, N);

H\_Tav = zeros(1,N); E\_Tav = zeros(1,N);

stdH\_T = zeros(1,N); stdE\_T = zeros(1,N);

for i = 1 : N

% nr of indents in file nr\_inds(i) = max(M(:,1,i));

% nr of cyles per indent nr\_cycs(i) = max(M(:,2,i));

% contact depth (list) dcl = M(:,4,i);

% load (list) PI = M(:,5,i);

% hardness (list) HI = M(:,6,i);

% reduced modulus (list) rml = M(:.7.i):

% voungs's modulus (list) El = rml.\*Edia.\*(1-ny\_mat^2)./(Edia-rml.\*(1-ndia^2));

% split column with data from all indents into lines and columns for j = 1 : nr\_inds\_max

Hr (:,j,i) = HI (1+(nr\_cycs\*(array(j)-1)):nr\_cycs\*array(j)); Er (:,j,i) = EI (1+(nr\_cycs\*(array(j)-1)):nr\_cycs\*array(j)); dcr(:,j,i) = dcl(1+(nr\_cycs\*(array(j)-1)):nr\_cycs\*array(j));

#### end

% skip single cycles

H(;;;i) = Hr (CycStartNr + 1 : nr\_cycs\_max;;i); E(;;;i) = Er( CycStartNr + 1 : nr\_cycs\_max;;i); dc(;;;i) = dcr(CycStartNr + 1 : nr\_cycs\_max;;i);

% data correction

H(:,:,i) = H(:,:,i) .\*corrH; E(:,:,i) = E(:,:,i) .\*corrE; dc(:,:,i) = dc(:,:,i) .\*corrdc;

 $\begin{array}{l} {\sf Last} = H(:,:,i).^*(dc(:,:,i).^2*AF\_old(1) + dc(:,:,i).^*AF\_old(2) + dc(:,:,i).^0.5.^*AF\_old(3)); \\ {\sf H\_new}(:,:,i) = {\sf Last}./(dc(:,:,i).^2*AF\_new(1) + dc(:,:,i).^*AF\_new(2) + dc(:,:,i).^0.5.^*AF\_new(3)); \end{array}$ 

for k = 1 : nr\_cycs(i) - CycStartNr

Hav (k,i) = mean(nonzeros(H (k,:,i))); Eav (k,i) = mean(nonzeros(E (k,:,i))); dcav(k,i) = mean(nonzeros(dc(k,:,i)));

stdH (k,i) = std(nonzeros(H (k,:,i))); stdE (k,i) = std(nonzeros(E (k,:,i))); stddc(k,i) = std(nonzeros(dc(k,:,i)));

H new av (k,i) = mean(nonzeros(H new (k,:,i))); stdH\_new\_av (k,i) = std(nonzeros(H\_new (k,:,i)));

end

H\_Tav(i) = mean(nonzeros(H(:,:,i))); E\_Tav(i) = mean(nonzeros(E(:,:,i)));

stdH\_T(i) = std(nonzeros(H(:,:,i))); stdE\_T(i) = std(nonzeros(E(:,:,i)));

end	
% display data % ====================================	
% plotting	
if stremp//off split) == 1	
61 - Series	
smp = 1.2; % figure size factor set(f1, 'Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp]);	
set(0,'defaultAxesFontName', font_n) set(0,'defaultTextFontName', font_n)	
% setting chart position in figure AxesH = axes('Units', 'normalized', 'Position', [0.10, 0.15, 0.75, 0.8]);	
[hAx,hLine1,hLine2] = plotyy(dcav,Hav,dcav,Eav); set(hLine1, 'color',cm1,'LineStyle','','LineWidth', llw_p1); set(hLine2, 'color',cm2, 'LineStyle','','LineWidth', llw_p1); hold on	
set(hAx(1),'YLim',[0 Hmax]); set(hAx(2),'YLim',[0 Emax], 'Visible','on'); set(hAx(1),'Xlim',xlim);	
<pre>for i = 1:N hErrb2 = errorbar(dcav(:,i), Eav(:,i)*AxCorr, vt, 'LineWidth', mlw_p1, 'Color',cm2, 'MarkerFaceColor', 'w'); errorbar_tick(hErrb2,eb_width); hErrb1 = errorbar(dcav(:,i), Hav(:,i), stdH(:,i)*std_os, 'o', 'LineWidth', mlw_p1, 'Color', cm1, 'MarkerFaceColor', 'w'); errorbar_tick(hErrb1,eb_width); end</pre>	
% Setting Tick and Limits set(hAx(1),'YLim',[0 Hmax]); set(hAx(2),'YLim',[0 Emax]); set(hAx(2),'YLim',[0 Emax]);	
set(hAx,'Xlim',xlim);	
% Adding Labels xl = xlabel(hAx(2),'Contact Depth [nm]', 'FontWeight', 'bold', 'FontSize', FontSize1); yl1 = ylabel(hAx(1), 'Hardness [GPa]', 'FontWeight', 'bold', 'FontSize',FontSize1); yl2 = ylabel(hAx(2), 'Youngs Modulus [GPa]', 'FontWeight', 'bold', 'FontSize',FontSize1);	
% Label Positioning xlabh = get(gca, XLabel'); set(xlabh,'Position',get(xlabh,'Position') - [0.3 0]) %set(yl1, 'Units', 'Normalized', 'Position', [-0.05, 0.5, 0]); set(yl2, 'Units', 'Normalized', 'Position', [1.11, 0.5, 0]);	
% Removing y1 Ticks on y2 set(hAx(1), <sup>B</sup> ox', <sup>c</sup> off') set(hAx(1), <sup>'</sup> XAxisLocation','top','XTickLabel',[])	
set(hAx(1),'linewidth',1.5,'FontSize',FontSize2); set(hAx(2),'linewidth',1.5,'FontSize2);	
set(hAx(1),'YColor',cm1); set(hAx(2),'YColor',cm2);	
gridcolor(gca,':',[1 1 0],{[0 0 0],'k',"})) grid on	
end de la constant de	
% PLOT 2: Harndess vs. Contact Depth	
if strcmp('on', split) == 1 && strcmp('on', HE_plot) == 1 f2 = figure;	
% setting chart position in figure AxesH = axes('Units', 'normalized', 'Position', [0.15, 0.15, 0.75, 0.8]);	
cm_p2 = cms;	
ter i - 7.81	

```
hObj = plot(dcav(:,i), Hav(:,i));
     hAx2 = gca;
     set(hObj, 'color', cm_p2(temps(i),:), 'LineStyle', '--', 'LineWidth', llw_p2, 'MarkerSize', 1);
     hold on
     if strcmp(AF_split, 'on') == 1
        hObj = plot(dcav(:,i), H_new_av(:,i));
hAx2 = gca;
        set(hObj, 'color', cm_p2(temps(i),:), 'LineStyle', '--', 'LineWidth', llw_p2, 'MarkerSize', 1);
     end
     hErrb = errorbar(dcav(:,i), Hav(:,i), stdH(:,i) * std_os, ms{temps(i)},...
        Line Vidith', mlw_p2, 'MarkerSize', mz p2,...
'MarkerEdgeColor', cm_p2(temps(i),:), 'MarkerFaceColor', 'w', 'Color', cm_p2(temps(i),:));
     if strcmp(AF_split, 'on') == 1
        hErrb = errorbar(dcav(:,i), H_new_av(:,i), stdH(:,i) * std_os, ms{temps(i)},...
           'LineWidth', mlw_p2, 'MarkerSize', mz_p2,...
'MarkerEdgeColor', cm_p2(temps(i),:), 'MarkerFaceColor', 'w', 'Color', cm_p2(temps(i),:));
     end
     errorbar_tick(hErrb,eb_width,'UNITS');
     hErrb = get(gca,'Children');
hErrb_sum(i)=hErrb(1);
     legend_str{i} = strcat(num2str(s_spec{temps(i)}));
     hold on
   end
  set(hAx2,'YLim',[0 Hmax]);
set(hAx2,'Xlim',xlim);
   % Adding Labels
   xl = xlabel(hAx2,'Contact Depth [nm]', 'FontWeight', 'bold',...
'FontSize',FontSize1');
  y1 = ylabel(hAx2, 'Hardness [GPa]', 'FontWeight', 'bold',...
'FontSize',FontSize1);
   % Label Positioning
   xlabh = get(gca,'XLabel');
  set(xlabh, 'Position',get(xlabh, 'Position') - [0.20])
set(y1, 'Units', 'Normalized', 'Position', [-0.1, 0.5, 0]);
   set(hAx2,'linewidth',1.5,'FontSize',FontSize2);
   set(hAx2,'linewidth',1.5,'FontSize',FontSize2);
   legend(hErrb_sum, legend_str, 'location', leg_pos_list{leg_pos});
  legendmarkeradjust(5,2)
  grid on
end
% PLOT 3: Young's Modulus vs. Contact Depth
if strcmp('on', YM_plot) == 1
  f3 = figure;
  % setting chart position in figure
AxesH = axes('Units', 'normalized', 'Position', [0.15, 0.15, 0.75, 0.8]);
  cm_p2 = cms;
  for i = 1:N
     hObj = plot(dcav(:,i), Eav(:,i));
     hAx2 = gca;
     set(hObj, 'color', cm_p2(temps(i),:), 'LineStyle', '--', 'LineWidth', llw_p2, 'MarkerSize', 1);
     hold on
     hErrb = errorbar(dcav(:,i), Eav(:,i), stdE(:,i) * std_os, ms{temps(i)},...

    'lineWidth', mlw_p2, 'MarkerSize', mz p2,...
    'MarkerEdgeColor', cm_p2(temps(i),:), 'MarkerFaceColor', 'w', 'Color', cm_p2(temps(i),:));

     errorbar_tick(hErrb,eb_width,'UNITS');
     hErrb = get(gca,'Children');
hErrb_sum(i)=hErrb(1);
     legend_str{i} = strcat(num2str(s_spec{temps(i)}));
     hold on
   end
```

```
set(hAx2,'YLim',[0 Emax]);
set(hAx2,'Xlim',xlim);
   % Adding Labels
   xl = xlabel(hAx2,'Contact Depth [nm]', 'FontWeight', 'bold',...
  'FontSize',FontSize1');
y1 = ylabel(hAx2, 'Youngs Modulus [GPa]', 'FontWeight', 'bold',...
      'FontSize',FontSize1);
  % Label Positioning
   xlabh = get(gca,'XLabel');
  set(xlabh,'Position',get(xlabh,'Position') - [0.2 0])
set(y1, 'Units', 'Normalized', 'Position', [-0.1, 0.5, 0]);
   set(hAx2,'linewidth',1.5,'FontSize',FontSize2);
  set(hAx2,'linewidth',1.5,'FontSize',FontSize2);
   legend(hErrb_sum, legend_str, 'location', leg_pos_list{leg_pos});
  legendmarkeradjust(5,2)
  grid on
end
% size effect
%
set(0,'defaultAxesFontName', font_n)
set(0,'defaultTextFontName', font_n)
if strcmp(ise, 'on') == 1
  if strcmp(AF_used, 'old') == 1
     H_used = H;
  else
     H_used = H_new;
  end
  n = 0;
  for i=1:size(H_used,2)
    if H_used(1,i,s_ise) ~= 0
        n = n + 1;
     end
   end
  H_ise = H_used(:, 1:n, s_ise);
  dc_ise = dc(:, 1:n, s_ise);
  [frs, gov] = ISE_fit1(1./dc_ise, H_ise.^2);
coefs(s_ise,:) = coeffvalues(frs);
  H0 = coefs(s_ise,1);
   hst = coefs(s_ise,2);
  dc_fit = [1 10^5];
Hq_fit = H0^2 + H0^2*hst.*1./(dc_fit);
  Yise = H_ise.^2 / H0^2;
Yise_fit = (Hq_fit / H0^2)';
   idc_ise_av = zeros(1, size(Yise,1));
  idc_ise_std = zeros(1, size(Yise,1));
  Yise_av = zeros(1, size(Yise,1));
Yise_std = zeros(1, size(Yise,1));
  for i = 1:length(Yise_av)
     idc_ise_av(i) = mean(1./dc_ise(i,:));
idc_ise_std(i) = std(1./dc_ise(i,:));
     Yise_av(i) = mean(Yise(i,:));
Yise_std(i) = std(Yise(i,:));
   end
   % plot
   f4 = figure;
  AxesH = axes('Units', 'normalized', 'Position', [0.12, 0.15, 0.8, 0.7]);
  p2 = plot(1./dc_fit, Yise_fit);
set(p2, 'LineStyle', '--', 'LineWidth', 3, 'Color', [0.5 0.5 0.5]);
  grid on
  hold on
```

p3 = ploterr(idc\_ise\_av, Yise\_av, 5.\*idc\_ise\_std, Yise\_std, 'o', 'hhx', 1.5); p3\_h = get(gca, 'Children');

set(p3, 'Color', 'k', 'LineWidth', 1.5, 'MarkerEdgeColor', 'k', 'MarkerFaceColor', [0.4 0.4 0.4], 'MarkerSize', 7];
ax1 = gca;
p_h = [p3(1) p2(1)];
if Y_ise_max == 0 set(ax1, 'ylim',[0 0.5 + ceil(max(Yise(:)))]) else set(ax1, 'ylim',[0 Y_ise_max]) end
set(ax1, 'xlim',[0 1/dcmin])
<pre>xlabel(ax1, '1 / dc [nm^-^1]', 'FontWeight', 'bold', 'FontSize',FontSize1) ylabel(ax1, 'H^ ^2 / H0^ ^2 [-]', 'FontWeight', 'bold', 'FontSize',FontSize1)</pre>
set(ax1, 'linewidth',1.5,'FontSize',FontSize2);
<pre>xAx2 = LinkTopAxisData(1./scale_dc,scale_dc,'dc [nm]'); % Add a top axis set(xAx2, 'linewidth',1.5,'FontSize',FontSize2);</pre>
xlabel(xAx2, 'dc [nm]', 'FontWeight', 'bold', 'FontSize',FontSize1)
leg = legend(p_h, {'data points' 'Nix-Gao Fit'}, 'location', 'NorthWest','Color', 'w','LineWidth',1.5); set(leg, 'Color', [0.98 0.98 0.98]);
annbox = annotation('textbox', [0.615 0.298 0.10 0.1], 'String', {[H^^2 / H_0^^2 = 1 + h^^* 1 / dc'], ]], [H_0 = 'num2str(round(H0*100)/100) 'GPa'], [h^^* = 'num2str(round(hst*1)/1) 'nm']], 'BackGroundColor',[0.98 0.98 0.98], 'FontSize',10, 'LineWidth',1.5, 'FontWeight', 'bold');
end
% directory management % ====================================
cd(ex_dir);

## Creep data analysis

close all
% file search
% ====================================
% file directory
p_dir = 'D:\Matlab Files';
% function file directory
f_dir = 'D:\Matlab Files\functions';
% data directory
d_dir = 'D:\Studium\Diplomarbeit\Nanoindentation\Data\Vergleiche\Dif Temperatures\Cr ufg\Creep Experiments\RT-300\raw data';
%export directory
ex dir = d dir;
%an_name = 'T5 Cr1IA lc100 dw200 6inds creep.txt':
% dwell data file name
dw name='cr1lA T19
% analysis settings 1
// a allalysis sectings 1
//
and the stand
spirt = on;
inds = 4;
array = [1 2 3 4];
Temps = [25 100 200 300];
temps_array = [1 2 3 5];
% experimental settings
%
load = [100]: % constand load [mN]
comp = [0.83.0.90.1.11.0.79]; % compliance: enter either one or all values
Some (Second and the second and the
Anomocr of indentitions
dwall = 200, % dwall period [s]
uwen - 200, // uwen periou [5]
a = 2.00. V latice parameter is approxim
a = 2.88; % lattce parameter in angsroem
% a(Cr) = 2.88 A ; a(Ta) = 3.30 A

	76 purgers vector to latice parameter
pu_corr = 1.1;	% pile up correction affecing absolute depth
% analysis settings 2 % ======	
,o	
init = 2; 9	6 number of header lines % first point used from data set
n_start = 2; n_end = 199;	% last point used from data set
length_sta = 20; length_sth = 198.	% length (in measured points) of stage a % points for fitting stage b
show_length_stb = 1	.00; % points used for stage b
cf = 2.8:	% constraint factor
u = 2.0,	
epsb = 0.75;	% geometry factor berkovic "epsilon"
sc = 1; 9	6 auxilary points for slope calculation
ash = 1;	
% indenter data	
70 ========	
% area function	
AF = [9173 2180 25.0	)9;
6360 2026 27.63;	
-9023 3650 26.37; -22609 4466 26.69	)];
AE list = [2 2 2 2].	
∩ı'_list = [2 2 2 3];	
% plot settings 1 % =======	
,	
vFig1 = 'off';	% absolute depth vs time
vFig3 = 'off';	% hardness vs time
vFig4 = 'off';	% In(Hardness) vs In(Strain Rate)(continous)
vFig5 = 'off'; vFig6 = 'off'	% In(Hardness) vs In(Strain Rate)(stage A & B) % strain rate sensitivity vs stress (diff fits)
vFig7 = 'off';	% strain rate sensivitity vs stress (stage A & B)
vFig8 = 'on';	% strain rate sensivitity vs stress (continous)
vFig9 = 'off'; vFig10= 'off'	% activation volume vs stress (stA, stA fit) % activation volume vs stress (continuus)
VIIGTO- OII ;	/ activation volume vs stress (conditious)
% plot settings 2	
% =========	101. % time range limite
har_pl_range = [0 20	; % hardness plotting limits
str_pl_range = [10^-	1 10^0]; % stress plotting limits
stn_pl_range = [10^-	13 10^-2];
vst_pl_range = [10^	) 10^3]; % activation volume plotting limits
· · ·	0/ euro line width
ıw = 1.5; fs = 14:	% axes line width % axes font size
fw = 'bold';	% axes font weight
fn = 'Calibri':	% axes font name
cm1 = lines(inds);	% colormap 1
cm1 = lines(inds); cm2 = [0.0 0.1 0.9;	% colormap 1
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0 0;	% colormap 1
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0;	% colormap 1
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0];	% colormap 1 % colormap 2
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off';	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = [0.0 0.1 0.9;	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 1.0 0.3 0.0;	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 1.0 0.3 0.0; 0.0 0.4 0.9:	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 1.0 0.3 0.0; 0.0 0.4 0.9; 0.0 0.6 0.9];	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 0.0 0.4 0.9; 0.0 0.6 0.9]; cm4 = [0.4 0.4 0.4];	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = $[0.0  cdot 1.0.9;$ 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = $[0.0  cdot 1.0.9;$ 0.7 0.1 0.0; 1.0 0.3 0.0; 0.0 0.4 0.9; 0.0 0.6 0.9]; cm4 = $[0.4  cdot 4.0.4];$ symb. list = $f_{10}^{11}$ to '10	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 1.0 0.3 0.0; 0.0 0.4 0.9; 0.0 0.4 0.9; 0.0 0.6 0.9]; cm4 = [0.4 0.4 0.4]; symb_list = {0,'0,'0	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 1.0 0.3 0.0; 0.0 0.4 0.9; 0.0 0.6 0.9]; cm4 = [0.4 0.4 0.4]; symb_list = {'0', '0', '0} log_spr = 0.06;	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 1.0 0.3 0.0; 0.0 0.4 0.9; 0.0 0.6 0.9]; cm4 = [0.4 0.4 0.4]; symb_list = {'0','0','0' log_spr = 0.06; smp = 1.2;	% colormap 1 % colormap 2 % special color map sef
<pre>cm1 = lines(inds); cm2 = [0.0 0.1 0.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; sp_cm_set = 'off'; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 1.0 0.3 0.0; 0.0 0.4 0.9; 0.0 0.6 0.9]; cm4 = [0.4 0.4 0.4]; symb_list = {'0','0','0' log_spr = 0.06; smp = 1.2; % import data %</pre>	% colormap 1 % colormap 2 % special color map sef
cm1 = lines(inds); cm2 = [0.0.010.9; 0.7 0.0 0.0; 1.0 0.3 0.0; 1.0 0.5 0.0; 1.0 0.7 0.0]; cm3 = [0.0 0.1 0.9; 0.7 0.1 0.0; 1.0 0.3 0.0; 0.0 0.4 0.9; 0.0 0.4 0.9; 0.0 0.6 0.9]; cm4 = [0.4 0.4 0.4]; symb_list = {0', '0', '0} log_spr = 0.06; smp = 1.2; % import data %	% colormap 1 % colormap 2 % special color map sef

```
Y7 = [0.0420 0.0204 0.0255 0.0668 0.0212 0.0331];
Y7_std = [0.0018 0.0017 0.0050 0.0122 0.0015 4.1400e-04];
Y9 = [21.7167 75.4126 50.5386 14.9109 17.9653 18.5539];
Y9_std = [0.9209 6.3986 8.5599 2.7753 2.7753 0.1485];
cd(d_dir);
dw_data = dlmread(dw_name);
cd(f_dir);
time_column = dw_data(:,1);
mdepth_column = dw_data(:,2);
% time
t = zeros(dwell-1,inds);
for i=1:inds
 t(:,i) = time_column(init+dwell*(i-1):init+i*dwell-2);
end
% gap between indenter and surface: hs
hs = zeros(inds,1);
if length(load) > 1
  if length(comp) > 1
     for i = 1:inds
        hs(i) = epsb * load(i) * comp(i);
     end
   else
     for i = 1:inds
hs = epsb * load(i) * comp(1);
  end
end
else
if length(comp) > 1
     for i = 1:inds
    hs(i) = epsb * load(1) * comp(i);
     end
   else
    for i = 1:inds
hs = epsb * load(1) * comp(1);
  end
end
end
 % absolute depth: ad
ad = zeros(dwell-1,inds);
for i=1:inds
  ad(:,i) = mdepth_column(init+dwell*(i-1):init+i*dwell-2);
end
%absolute depth corrected: adc
adc = zeros(dwell-1,inds);
for i=1:inds
  try
     adc(:,i) = ad(:,i) - hs(i);
  catch
     adc(:,i) = ad(:,i) - hs(1);
   end
 end
adc = adc.*pu_corr; %pile-up correction step
len = length(ad(:,1));
% smallest corrected depths h0c
h0c = zeros(inds,1); % hs corrected indenter depth at start of dwell time
for i=1:inds
  h0c(i) = min(adc(:,i));
end
% relative depth corrected rdc
rdc = zeros(len,inds);
for i = 1:inds
  for j = 1:len
     rdc(j,i) = adc(j,i)- h0c(i);
   end
 end
% fitting curves (with "creep_fit()" function)
 % ===
Xs = zeros(n_end - n_start + 1, inds);
Ys = zeros(n_end - n_start + 1, inds);
for i=1:inds
  Xs(:,i) = t (n_start : n_end, i);
```

```
Ys(:,i) = rdc(n_start : n_end, i);
 end
range_stb = length(Xs)-length_stb +1 : length(Xs);
coefs = zeros(inds,4);
coefs_sta = zeros(inds,4);
coefs_stb = zeros(inds,4);
for i=1:inds

      [frs, gov]
      = creep_fit_res1(Xs(:,i),Ys(:,i));

      coefs(i.:)
      = coeffvalues(frs);

      [frs, gov]
      = creep_fit_res1(Xs(1:length_sta,i), Ys(1:length_sta,i));

    coefs_sta(i,:) = coeffvalues(frs);
[frs, gov] = creep_fit_res1(Xs(range_stb,i),Ys(range_stb,i));
     coefs_stb(i,:) = coeffvalues(frs);
        = zeros(n_end - n_start + 1, inds); % fit of corr. relative depths
Yf sta = zeros(length sta, inds);
Yf_stb = zeros(length_stb, inds);
for i=1:inds
    Yf(;,i) = coefs (i,1).*(Xs(:,i) - coefs (i,2)).^(coefs (i,3)) + coefs (i,4).*Xs(:,i);
Yf_sta(:,i) = coefs_sta(i,1).*(Xs(1:length_sta,i)- coefs_sta(i,2)).^(coefs_sta(i,3)) + coefs_sta(i,4).*Xs(1:length_sta,i);
    \label{eq:constraint} Yf_stb(:,i) = coefs_stb(i,1).*(Xs(range_stb,i) - coefs_stb(i,2)).^{(coefs_stb(i,3))} + coefs_stb(i,4).*Xs(range_stb,i); \\ (Xs(range_stb,i) - coefs_stb(i,2)).
end
 %% calculating data
 %
 % fitted abolute dephts: adf
adf = zeros( n_end - n_start + 1, inds);
adf_sta = zeros(length_sta, inds);
adf_stb = zeros(length_stb, inds);
for i=1:inds
adf(:,i) = Yf(:,i) + h0c(i);
    adf_sta(:,i) = Yf_sta(:,i) + hOc(i);
adf_stb(:,i) = Yf_stb(:,i) + hOc(i);
 end
 % derivated fitted absolute depths: d_adf
d_adf = zeros(n_end - n_start + 1, inds);
d_adf_sta = zeros(length_sta, inds);
d_adf_stb = zeros(length_stb, inds);
for i=1:inds
     \begin{array}{l} d_{adf} : (;i) = coefs \ (i,1)^*coefs \ (i,3)^*(Xs(:,i) \ -coefs \ (i,2))^{-k} (coefs \ (i,3)^{-1}) + coefs(i,4); \\ d_{adf} : sta(:,i) = coefs \_ sta(i,1)^*coefs \_ sta(i,3)^*(Xs(1:length\_sta,i) - coefs \_ sta(i,2))^{-k} (coefs \_ sta(i,3)^{-1}) + coefs \_ sta(i,4); \\ d_{adf} \_ stb(:,i) = coefs \_ stb(i,1)^*coefs \_ stb(i,3)^*(Xs(range\_stb,i) \ -coefs \_ stb(i,2))^{-k} (coefs \_ stb(i,3)^{-1}) + coefs \_ stb(i,4); \\ \end{array} 
 end
 % derivated absolute depth : d_ad
d_ad = zeros(n_end - n_start + 1 - asp , inds);
for i = 1:inds
    for j = 1:length(d ad)
        d_ad(j,i) = (adc(j + asp, i) - adc(j, i))/(Xs(j + asp, i) - Xs(j, i));
    end
end
 % strain rate
d_epsf = zeros(n_end - n_start + 1, inds);
d_epsf_sta = zeros(length_sta, inds);
d_epsf_stb = zeros(length_stb, inds);
for i=1:inds
    d_epsf (:,i) = d_adf (:,i)./adf (:,i);
d_epsf_sta(:,i) = d_adf_sta(:,i)./adf_sta(:,i);
d_epsf_stb(:,i) = d_adf_stb(:,i)./adf_stb(:,i);
 end
d_eps = zeros(n_end - n_start + 1 - asp, inds);
for i=1:inds
    for j=1:length(d_eps)
    d_eps(j,i) = d_ad(j,i)./adc(j,i);
     end
end
% logarithm of d eps
log_d_epsf = zeros(n_end - n_start + 1, inds);
 log_d_epsf_sta = zeros(length_sta, inds);
log_d_epsf_stb = zeros(length_stb, inds);
 for i=1 inds
    for j=1:(n_end - n_start + 1)
         log_d_epsf (j,i) = log(d_epsf (j,i));
     end
```

```
for j=1:length_sta
    log_d_epsf_sta(j,i) = log(d_epsf_sta(j,i));
   end
  for j=1:length_stb
    log_d_epsf_stb(j,i) = log(d_epsf_stb(j,i));
  end
end
log_d_eps = zeros(n_end - n_start + 1 - asp, inds);
for i=1:inds
  for j=1:(n_end - n_start + 1 - asp)
    log_d_eps(j,i) = log(d_eps(j,i));
end
end
% contact area
Acf = zeros(n_end-n_start + 1, inds);
Acf_sta = zeros(length_sta, inds);
Acf_stb = zeros(length_stb, inds);
Ac = zeros(n_end-n_start + 1, inds);
for i=1:inds
  for j=1:(n_end-n_start + 1)
   end
  + AF(AF_list(i),3).*adf_sta(j,i).^2;
  end
   \begin{array}{l} \mbox{for } j=1:\mbox{length\_stb} \\ \mbox{Acf\_stb}(j,i) = AF(AF\_list(i),1) *adf\_stb(j,i).^0.5 + AF(AF\_list(i),2).*adf\_stb(j,i)... \\ + AF(AF\_list(i),3).*adf\_stb(j,i).^2; \end{array} 
  end
end
acsr = zeros(n_end-n_start + 1 - asp, inds);
for i=1 inds
  for j=1:(n_end-n_start + 1 - asp)
    acsr(j,i) = AF(AF_list(i),1)*adc(j,i).^0.5 + AF(AF_list(i),2).*adc(j,i)...
+ AF(AF_list(i),3).*adc(j,i).^2;
  end
end
% strain
Hf = zeros(n_end - n_start + 1, inds);
Hf_sta = zeros(length_sta, inds);
Hf_stb = zeros(length_stb, inds);
H = zeros(n_end - n_start + 1, inds);
if length(load) > 1
for i=1:inds
      \begin{array}{ll} H_{i}(j_{i}) &= load(i)^{*}10^{-(3)}/(Acf & (j,i)^{*}10^{-(12)})^{*}10^{-(3)}; \\ H_{i}(j_{i}) &= load(i)^{*}10^{-(3)}/(Ac & (j,i)^{*}10^{-(12)})^{*}10^{-(3)}; \\ \end{array} 
     end
    for j=1:length_sta
       Hf_sta(j,i) = load(i)*10^(-3)/(Acf_sta(j,i)*10^(-12))*10^(-3);
    end
    end
  end
 else
  for i=1:inds
    end
    for j=1:length_sta
       Hf_sta(j,i) = load(1)*10^(-3)/(Acf_sta(j,i)*10^(-12))*10^(-3);
     end
     for j=1:length_stb
       Hf_stb(j,i) = load(1)*10^(-3)/(Acf_stb(j,i)*10^(-12))*10^(-3);
     end
  end
```

log\_Hf = log(Hf); log\_H = log(H); log\_Hf\_sta = log(Hf\_sta); log\_Hf\_stb = log(Hf\_stb); Stress = Hf /cf; Stress\_sta = Hf\_sta/cf; Stress\_stb = Hf\_stb/cf; Stress\_av\_sto = zeros(length(array),1); Stress\_av\_sta = zeros(length(array),1); Stress\_av\_stb = zeros(length(array),1); for i=1:length(array) Stress\_av\_sto(i,1) = mean(Stress(1:length\_sta,array(i))); Stress\_av\_sta(i,1) = mean(Stress\_sta(:,array(i))); Stress av stb(i,1) = mean(Stress stb(:,array(i))); end Stress\_std\_sto = std(Stress\_av\_sto); Stress\_std\_sta = std(Stress\_av\_sta); Stress\_std\_stb = std(Stress\_av\_stb); log\_Stress = log(Stress); log\_Stress\_sta = log(Stress\_sta); log\_Stress\_stb = log(Stress\_stb); % m-values ms = zeros(n\_end - n\_start + 1 - sc, inds); m\_sta = zeros(length\_sta, inds); m\_stb = zeros(length\_stb, inds); for i = 1:inds  $\label{eq:constant} \begin{array}{l} \mbox{for $j=1:(n_end - n_start + 1 - sc)$} \\ \mbox{ms}(j,i) = (log_Stress(j+sc,i)-log_Stress(j,i))/(log_d_epsf(j+sc,i)-log_d_epsf(j,i)); \\ \end{array}$ end for j = 1:length\_sta - sc  $\label{eq:m_sta} m\_sta(j,i) = (log\_Stress\_sta(j+sc,i)-log\_Stress\_sta(j,i))/(log\_d\_epsf\_sta(j+sc,i)-log\_d\_epsf\_sta(j,i));$ end for j = 1:length\_stb - sc  $m_stb(j,i) = (log_stress_stb(j+sc,i)-log_stress_stb(j,i))/(log_d_epsf_stb(j+sc,i)-log_d_epsf_stb(j,i));$ end end % stage a/b linear fitting ٥/ log\_d\_epsfl\_stb = log\_d\_epsf(range\_stb, :);  $\label{eq:log_Hfl_stb} $$ log_Hfl_stb = log_Hf(range_stb, :);$$ show_range_stb = length(log_d_epsf_stb) - show_length_stb : length(log_d_epsf_stb);$$$ coefs\_lin = zeros(length(array),2); % stage a fit out of single fit coefs\_sta\_lin = zeros(length(array),2); % stage a fit out of stage a fit coefs\_stb\_lin = zeros(length(array),2); % stage b fit out of single fit 

 std\_coefs\_lin
 = zeros(length(array),1); % goodnes of fit of coefs\_lin

 std\_coefs\_sta\_lin
 = zeros(length(array),1); % goodnes of fit of coefs\_lin

 std\_coefs\_stb\_lin
 = zeros(length(array),1); % goodnes of fit of coefs\_lin

 for i=1:inds [frs, gov] = stage\_linfit\_1(log\_d\_epsf(1:length\_sta, i),log\_Hf(1:length\_sta, i)); coefs lin(i,:) = coeffvalues(frs); std\_coefs\_lin(i) = gov.rmse; ista\_coers\_initi/ = gov.rinse, [frs, gov] = stage\_linfit\_1(log\_d\_epsf\_sta(:, i),log\_Hf\_sta(:, i)); coefs\_sta\_lin(i,:) = coeffvalues(frs); std\_coefs\_sta\_lin(i) = gov.rmse; [frs, gov] = stage\_linfit\_1(log\_d\_epsf\_stb(show\_range\_stb, i),log\_Hf\_stb(show\_range\_stb, i)); coefs\_stb\_lin(i,:) = coeffvalues(frs); std\_coefs\_stb\_lin(i) = gov.rmse; end % disp('SRS Stage A, fit 200s') % disp(coefs lin(:,1)); m\_av\_sto = mean(coefs\_lin(array,1)); m std sto = std(coefs lin(array,1)); % disp('SRS Stage A, fit stA') % disp(coefs\_sta\_lin(:,1)); m\_av\_sta = mean(coefs\_sta\_lin(array,1)); m\_std\_sta = std(coefs\_sta\_lin(array,1)); % disp('SRS Stage B, fit stB') % disp(coefs\_stb\_lin(:,1));

1

n_av_stb = mean(coefs_stb_lin(array,1)); n_std_stb = std(coefs_stb_lin(array,1));
6% Calculating V*
6
rs = zeros(n_end - n_start + 1 - sc, inds); rs_sta = zeros(inds, 1);
or i = 1:inds
for j = 1:(n_end - n_start + 1 - sc) vs(j,i) = 3 ^ 0.5 * 1.3807*10^-23 * (Temps(i) + 272.23) * cf / (Hf(j,i) * 10^9 * ms(j,i)) / ((a/2 * k * 10^-10)^3); end
vs_sta(i) = 3 ^ 0.5 * 1.3807*10^-23 * (Temps(i) + 272.23) * cf / ((mean(Hf_sta(:,array(i))) * 10^9 * coefs_sta_lin(array(i),1))) / ((a/2 * k * 10^-10)^3);
ind
6% plotting curves
6 ====================================
s setting tonts et(0,'defaultAxesFontName', fn) et(0,'defaultTextFontName', fn)
6 seetting color map f strcmp('on',split) == 1; .cm = cm2:
ise cm = cm1:
nd f strcmp('on', sp_cm_set) == 1; cm = cm3; nd
6 FIGURE 1: Absolute Depth vs. Time
1=figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig1);
or i=1:length(array)
<pre>l1 = plot(Xs(:,array(i)), adc(1:length(Xs),array(i)), 'linewidth', 2.0, 'color', cm(temps_array(i),:)); h_11 = get(gca,'Children'); hold on</pre>
h_fit(i)=h_l1(1);
<pre>if strcmp(split,'on') == 1 legend_str{i} = strcat(num2str(Temps(i)), '*C'); else</pre>
legend_str{i} = strcat('Indent', '#', num2str(array(i))); end
nd
iAx1 = gca;
et(hAx1, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs);
label( 'Time [s]', 'FontWeight', 'bold'); label( 'Absolute Depth [nm]', 'FontWeight', 'bold');
xis{[0,200,0,1200]};
egend(h_fit,legend_str,'location','SouthEast');
6 FIGURE 2: Relative Depth - Time
2=figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig2);
_fit = zeros(length(array),1);
or i=1:length(array) I1 = plot(Xs(;,array(i)),Ys(;,array(i)),'color',cm(temps_array(i),:)); set(I1(1),'linewidth',1.5); hold on I2 = plot(Xs(1:length_sta,array(i)),Yf_sta(:,array(i)),'color',cm(temps_array(i),:),'LineStyle','*','linewidth',1); h_I2 = get(gca,'children'); I3 = plot(Xs(range_stb,array(i)),Yf_stb(:,array(i)),'color',cm(temps_array(i),:),'LineStyle','-,','linewidth',2); h_I3 = get(gca,'Children');
h_fit(i)=h_l1(1);
if stremp(split los) = 1

```
legend_str{i} = strcat(num2str(Temps(i)), ' °C');
     legend_str{i} = strcat('Indent', '#', num2str(array(i)));
   end
end
hAx2 = gca;
set(hAx2, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs);
%axis([-5,200,-1,50]);
xlabel( 'Time [s]', 'FontWeight', 'bold');
ylabel( 'Relative Depth [nm]', 'FontWeight', 'bold' );
legend(h_fit,legend_str,'location','Northwest');
grid on;
% FIGURE 3: Hardness vs. Time --
f3 = figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig3);
for i=1:length(array)
  l1 = plot(Xs(:,array(i)), H(:,array(i)),...
      'linewidth',2.0,'color',cm(temps_array(i),:));
  hold on
  h_l1 = get(gca,'Children');
hold on
  h_fit(i)=h_l1(1);
  if strcmp(split, 'on') == 1
     legend_str{i} = strcat(num2str(Temps(i)),' °C');
   else
     legend_str{i} = strcat('Indent', '#', num2str(array(i)));
   end
end
hAx3 = gca;
set(hAx3, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs);
xlabel( 'Time [s]','FontWeight', 'bold');
ylabel( 'Harndess [GPa]','FontWeight', 'bold');
axis([tim_pl_range har_pl_range]);
legend(h_fit,legend_str,'location','NorthEast');
% FIGURE 4: In(Harndess) vs. In(Strain Rate)
f4 = figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig4);
for i=1:length(array)
  plot(log_d_epsf(1:length(log_Hf),array(i)),log_Hf(:,array(i)),...
'-o', 'color', cm(temps_array(i),:), 'linewidth', 1.0, 'markersize', 3)
   hold on
  h_l1 = get(gca,'Children');
h_fit(i)=h_l1(1);
   if strcmp(split.'on') == 1
    legend_str{i} = strcat(num2str(Temps(i)),' °C');
   else
     legend_str{i} = strcat('Indent', '#', num2str(array(i)));
   end
end
hAx4 = gca;
set(hAx4, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs);
xlim([-13 0]);
xiiii([150]),
ylim([min(log_Hf_stb(:)) - 0.3 max(log_Hf_sta(:)) + 0.2]);
%ylim([-0.6 0.6]);
axis([xlim ylim]);
xlabel(horzcat('ln (Strain Rate)'), 'FontWeight', 'bold');
ylabel(horzcat('ln (Hardness)'), 'FontWeight', 'bold');
legend(h_fit,legend_str,'location','West');
legendmarkeradjust(4, 1.5)
 grid <mark>on</mark>;
```

```
-87-
```

```
% FIGURE 5: In(Hardness) - In(Strain Rate) "Stage A, Stage B"--
f5 = figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig5);
for i=1:length(array)
    plot(log_d_epsf_sta(:,array(i)),log_Hf_sta(:,array(i)),...
   -o', 'oolor', cm(temps_array(i),:), 'linewidth', 1.0, 'markersize', 3)
hold on
   h l1 = get(gca,'Children');
   plot(log_d_epsf_stb(show_range_stb, array(i)),log_Hf_stb(show_range_stb ,array(i)),...
      's', 'color', cm(temps_array(i),:), 'linewidth', 1.0, 'markersize', 3)
   h_fit(i)=h_l1(1);
   if strcmp(split,'on') == 1
     legend\_str{i} = strcat(num2str(Temps(i)), ' ^C');
   else
     legend_str{i} = strcat('Indent', '#', num2str(array(i)));
   end
end
hAx5 = gca;
set(hAx5, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs);
xlabel(horzcat('ln (Strain Rate)'), 'FontWeight', 'bold');
ylabel(horzcat('ln (Hardness)'), 'FontWeight', 'bold');
legend(h_fit,legend_str,'location','SouthEast');
legendmarkeradjust(4, 1.5)
grid on;
% FIGURE 6: Strain Rate Sensitivity vs. Strain Rate Stage A/B ----
f6 = figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig6);
for i=1:length(array)
  loglog(mean(Stress(1:length_sta,array(i))), coefs_lin(array(i),1),...
           color',cm(temps_array(i),:), 'linewidth', 1.5)
  hold on
   loglog(mean(Stress_sta(:,array(i))), coefs_sta_lin(array(i),1),...
        o','color',cm(temps_array(i),:), 'linewidth', 1.5)
   hold on
   loglog(mean(Stress_stb(:,array(i))), coefs_stb_lin(array(i),1),'v',...
        color',cm(temps_array(i),:), 'linewidth', 1.5)
  hold on
if strcmp(split,'off') == 1
  errorbar(mean(Stress_av_sto), m_av_sto, m_std_sto,...
'+','color', 'k', 'markersize', 5.0, 'linewidth', 1.5)
   errorbar(mean(Stress_av_sta), m_av_sta, m_std_sta, 'o','color', 'k', 'markersize', 5.0, 'linewidth', 1.5)
  errorbar(mean(Stress_av_stb), m_av_stb, m_std_stb,..
'v','color', 'k', 'markersize', 5.0, 'linewidth', 1.5)
   hold on
  annotation('textbox', [0.20 0.14 0.3 0.3], 'String',...
{['STO'' m = ' num2str(m_av_sto)' +/-' num2str(m_std_sto)],...
['STA'' m = ' num2str(m_av_sta)' +/- ' num2str(m_std_sta)],...
['STB'' m = ' num2str(m_av_stb)' +/-' num2str(m_std_stb)]}...
    'BackGroundColor',[1.0, 1.0, 1.0],...
   'FontSize'.7):
end
hAx8 = gca;
set(hAx8, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs);
xlim([min(Stress_stb(:)) - 0.01 max(Stress_sta(:)) + 0.01]);
axis([xlim ylim]);
xlabel('Stress [GPa]','FontWeight', 'bold');
ylabel('Strain Rate Sensitivity [-]','FontWeight', 'bold');
grid on;
% FIGURE 7: Strain Rate Sensitivity vs. Strain Rate Stage A detailed ------
if strcmp (vFig7,'on') == 1
   f7 = figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp], 'visible', vFig7);
   for i=1:length(array)
```

```
loglog(X7(i), Y7(i),'-')
      hold on
   end
   loglog(X7,Y7,'LineWidth', 1.5, 'LineStyle', '--', 'Color', 'k');
  \label{eq:constraint} \begin{array}{l} \mbox{for i=1:length(array)} \\ \mbox{h7 = ploterr(X7(i), Y7(i), [], Y7\_std(i), strcat('k-', symb\_list{i}));} \end{array}
     h_l1 = get(gca,'Children');
      h_fit(i)=h_l1(1);
      set(h7,'Line
                     Width', 1.5, 'MarkerEdgeColor', 'k', 'MarkerFaceColor', cm(temps_array(i),:), 'MarkerSize', 10);
        if strcmp(split, 'on') == 1
legend_str{i} = strcat(num2str(Temps(i)), ' °C');
        end
   end
   loglog(X7,Y7,'k.');
   if strcmp(split, 'off') == 1
     errorbar(mean(Stress_av_sto), m_av_sto, m_std_sto,...
     '+','color', 'k', 'markersize', 5.0, 'linewidth', 1.5)
errorbar(mean(Stress_av_sta), m_av_sta, m_std_sta,...
     'o','color', 'k', 'markersize', 5.0, 'linewidth', 1.5)
errorbar(mean(Stress_av_stb), m_av_stb, m_std_stb,...
     'v','color', 'k', 'markersize', 5.0, 'linewidth', 1.5)
hold on
      annotation('textbox', [0.20 0.14 0.3 0.3], 'String',
      [[ST0''m = 'num2str(m_av_sto) '+/- 'num2str(m_std_sto)],...
[[STB''m = 'num2str(m_av_sta) '+/- 'num2str(m_std_sta)],...
[[STB''m = 'num2str(m_av_stb) '+/- 'num2str(m_std_stb)]},...
      'BackGroundColor',[1.0, 1.0, 1.0],...
      'FontSize',7);
   end
  hAx7 = gca;
set(hAx7, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs);
   vlim(srs pl range);
   xlim([min(X7) / 10^log_spr max(X7) * 10^log_spr]);
   xlabel('Stress [GPa]','FontWeight', 'bold');
   ylabel('Strain Rate Sensitivity [-]','FontWeight', 'bold');
  legend(h_fit, legend_str, 'location', 'SouthWest');
legendmarkeradjust(5, 1);
  grid on;
end
% FIGURE 8 : SRS vs. Stress Plot continous ----
f8 = figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig8);
for i=1:length(array)
  l1 = loglog(Stress(1:length(ms),array(i)),ms(:,array(i)),...
  'color, cm(temps_array(i),:), linewidth', 1.0, 'linestyle', symb_list{i}, 'markersize',3);
h_11 = get(gca,'Children');
   hold on
   h_fit(i)=h_l1(1);
   if strcmp(split,'on') == 1
     legend_str{i} = strcat(num2str(Temps(i)),' °C');
   else
     legend str{i} = strcat('Indent', '#', num2str(array(i)));
   end
end
hAx8 = gca;
set(hAx8, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs,...
     xLim', str_pl_range, 'yLim', srs_pl_range);
xlabel('Stress [GPa]','FontWeight', 'bold');
ylabel('Strain Rate Sensitivity [-]','FontWeight', 'bold');
legend(h fit,legend str,'location','SouthWest');
legendmarkeradjust(4, 2);
grid on;
% FIGURE 9: Activation Volume vs. Stress ----
if strcmp (vFig9,'on') == 1
```

```
f9 = figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp], 'visible', vFig9);
   X9 = X7;
   for i=1:length(array)
     loglog(X9(i), Y9(i), '--')
hold on
   end
   loglog(X9,Y9,'LineWidth', 1.5, 'LineStyle', '--', 'Color', 'k');
   for i=1:length(array)
h9 = ploterr(X9(i), Y9(i),[], Y9_std(i),strcat ('k-', symb_list{i}));
     h_l1 = get(gca, 'Children');
h_fit(i)=h_l1(1);
      set(h9,'LineWidth', 1.5, 'MarkerEdgeColor', 'k', 'MarkerFaceColor',cm(temps_array(i),:), 'MarkerSize', 10);
        if strcmp(split,'on') == 1
         legend_str{i} = strcat(num2str(Temps(i)),' °C');
        end
   end
   loglog(X9,Y9,'k.');
   hAx7 = gca;
set(hAx7, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs);
   vlim(vst pl range);
   xlim([min(X7) / 10^log_spr max(X7) * 10^log_spr]);
   xlabel('Stress [GPa]','FontWeight', 'bold');
ylabel('Activation Volume [b^3]','FontWeight', 'bold');
   legend(h_fit, legend_str, 'location', 'NorthWest');
legendmarkeradjust(5, 1);
   grid on;
end
% FIGURE 10: Activation Volume vs. Stress (continous) --
f10 = figure('Units', 'normalized', 'Position', [0.3, 0.3, 0.3*smp, 0.4*smp], 'visible', vFig10);
for i=1:length(array)
   l1 = loglog(Stress(1:length(vs),array(i)),vs(:,array(i)),...
   'color', cm(temps_array(i),:), 'linewidth', 1.0, 'linestyle', symb_list{i}, 'markersize',3); h_l1 = get(gca, 'Children');
   hold on
   h_fit(i)=h_l1(1);
   if strcmp(split, 'on') == 1
     legend_str{i} = strcat(num2str(Temps(i)), ' °C');
   else
     legend_str{i} = strcat('Indent', '#', num2str(array(i)));
   end
 end
hAx10 = gca;
set(hAx10, 'LineWidth', lw, 'FontWeight', 'normal', 'FontSize', fs,...
   'xLim', str_pl_range, 'yLim', vst_pl_range);
grid on;
xlabel('Stress [GPa]','FontWeight', 'bold');
ylabel('Activation Volume [b^3]','FontWeight', 'bold');
legend(h_fit,legend_str,'location','SouthWest');
legendmarkeradjust(4, 2);
 %% Data Display
m_range = zeros(length(array), 3);
 v_range = zeros(length(array), 3);
for i = 1:length(array)
m_range(i,1) = Temps(i);
m_range(i,2) = min(ms(:,i));
m_range(i,3) = max(ms(:,i));
 end
for i = 1:length(array)
   v_range(i,2) = Temps(i);
v_range(i,2) = min(vs(:,i));
   v_range(i,3) = max(vs(:,i));
 end
```

disp('SRS RANGE'); disp(' T['C] MIN MAX'); disp(m_range);
disp('');
disp('V* RANGE'); disp(' T['C] MIN MAX'); disp(v_range);
% ====================================

## Pop-In analysis

	-
clear all	
% file search	
%	
70	
a interaction dir. = 'D'.\Matlab Eiles\functions':	
Widata directory	
volate un eccory	
Inc_Un - C. Studium Diploma Dell'Inanominentation Data (CISXS) Data (hysteresis Data ,	
we die _ Dukter die wie binderscheit Maneindersteine Date (CEW2)	
The name its (rsw3 in Curi 24 and 7200, hefore bys tyt)	
inc_nume = 15 class logicit 24 binds 1200_belore hysickey	
% analysis information	
%	
array = [1 2 5 6]:	
nrofin = 5. % total number of indents in the schedule	
nrofcy = 8: % number of branches per cycle	
start_cvcle = 1:	
end cycle = 1:	
au skip = 3:	
au slope = 1:	
x jump boarder = 6;	
r over = 0; % tip radius over rule is off when r over is set to zero	
artifical x corr = 0;	
Er = 233; %[GPa]	
G = 115; %[GPa]	
%GCr = 115 GPa	
%GTa = 69 GPa	
% plotting properties 1	
%	
x_gap_Fig3 = 5; % gap on x axis in chart 3 between fitting curves	
y_gap_Fig3 = 1.5; % gap on y axis in chart 3 in perc for chart	
VHg1 = 'on';	
vFig2 = off;	
VHg3a = 00);	
VHigsb = Off;	
VFIg4 = OT;	
usp_ino - on,	
smp = 1 % figure size factor	
one a) to report out to too	
cm = [0 0 0 0 0 0]	
1,0,0,0,0:	
050500	
0.01.00.0:	
0.005.05	
0.00.10	
0.2.0.2.0.2:	
0.3 0.3 0.3]:	
······	
%% import & analyzing	
%	
cd(file_dir);	
_file_data = dlmread(file_name);	



```
x_pop = zeros(1, length(array));
y_pop = zeros(1, length(array));
for i = 1:length(array)
x_pop(i) = X(dX_max_pos(i) + x_jump_boarder, i)...
  - X(dX_max_pos(i) - x_jump_boarder, i);
y_pop(i) = Y(dX_max_pos(i),i);
end
% pop-in fit
try
  [fitresult, gov] = popin_linfit_1(x_pop,y_pop);
   coef_lin = coeffvalues(fitresult);
catch
   coef_lin = [0 0];
end
xf = [0 200];
yf = coef_lin(1).*xf + coef_lin(2);
% hertzian fitting of elastic loading part
Xe = zeros(max(dX_max_pos), length(array));
Ye = zeros(max(dX_max_pos), length(array));
for i=1:length(array)
    for j = 1 : dX_max_pos(i) - au_skip
      if X(1,i) >= 10
      Xe(1,i) = 0;
end
      if X(j,i) >= 0
         Xe(j,i) = X(j,i);
Ye(j,i) = Y(j,i);
      else
Xe(j,i) = 0;
         Ye(j,i) = 0;
      end
   end
end
Xe = Xe + artifical_x_corr;
Xe_p15 = Xe.^1.5;
coef_tip = zeros(1,length(array));
coef_tip_aux = zeros(1,length(array));
tip_fit_gov = cell(1,length(array));
yf_tip = zeros(length(Xe),length(array));
for i=1:length(array)
   Xeh = Xe(:.i):
   Xeh = Xeh(Xeh~=artifical_x_corr);
   Yeh = Ye(1:length(Xeh),i);
   if Yeh(1) == 0
      Yeh = Yeh(2:length(Yeh));
Xeh = Xeh(2:length(Xeh));
   end
   [fitres, gov] = tip_fit_7(Xeh, Yeh);
   coef_aux = coeffvalues(fitres);
   coef_tip(:,i) = coef_aux(1);
coef_tip_aux(:,i) = coef_aux(2);
tip_fit_gov{i} = gov;
   \label{eq:constraint} \begin{array}{l} for \ j=1:length(Xe) \\ \gamma f\_tip(j,i)=coef\_tip(i)^*(Xe(j,i)+coef\_tip\_aux(i))^{1.5}; \\ end \end{array}
end
coef_tip_av = mean(coef_tip);
coef_tip_std = std(coef_tip);
coef_tip_aux_av = mean(coef_tip_aux);
coef_tip_aux_std = std(coef_tip_aux);
% indenter tip radius calculation
tip_rad = zeros(1,length(array));
for i=1:length(array)
tip_rad(i) = (0.75*coef_tip(1,i)/(Er*10^9)*10^10.5)^2 * 10^9; % [nm]
```

```
if r_over ~= 0
tip_rad(:) = r_over;
end
tip_rad_av = mean(tip_rad(tip_rad~=0));
tip_rad_std = std(tip_rad(tip_rad~=0));
 css = zeros(1,length(array));
\label{eq:constraint} \begin{split} & constraint} constraints co
end
 rel_str = css.*10^-9./(G/(2*pi));
 %% show data
 % ==
if strcmp(disp_info, 'on') == 1
      disp('Pop-In Experiment Fitting Results of ');
      disp(strcat("", file_name, ""));
      P_popin = y_pop
P_popin_av = mean(y_pop)
P_popin_std = std(y_pop)
      CSS
      css_av = mean(css)
      css_std = std(css)
      rel_str
rel_str_av = mean(rel_str)
      rel_str_std = std(rel_str)
     coef_tip
% coef_tip_av
% coef_tip_std
coef_tip_aux
      % coef_tip_aux_av
% coef_tip_aux_std
     celldisp(tip_fit_gov)
     tip_rad
tip_rad_av
      tip_rad_std
 end
 mean(coef_tip)
mean(coef_tip_aux)
 %% Plotting
                                                                                                              ------
f1 = figure('Units', 'normalized', 'Position',...
[0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig1);
for i=1:length(array)
      pl_X = X(:,i);
      pl_X = pl_X(pl_X~=0);
      pl_Y = Y(:,i);
      pl_Y = pl_Y(pl_Y~=0);
     p1 = plot(pl_X, pl_Y,'b');
h_p1 = get(gca,'Children');
hold on
    p2 = plot(X((dX_max_pos(i) - x_jump_boarder),i), y_pop(i),'ro',...
'MarkerSize',5,'LineWidth',2); %plotting lower boarder
h_p2 = get(gca,'Children');
      plot(X((dX_max_pos(i) + x_jump_boarder),i) ,y_pop(i),'ro',...
             'MarkerSize',5,'LineWidth',2); %plotting upper boarder
      grid on
 end
h_fig = gca;
set(h_fig, 'LineWidth', 1.5, 'FontWeight', 'normal', 'FontSize', 12);
 hleg_1 = [h_p1(1), h_p2(1)];
legend(hleg_1,'load-depth data', 'pop-in marker','Location','SouthEast');
title (horzcat('L-D Hysterersis'),...
                  ntSize',10,'FontWeight', 'normal');
```

```
xlabel('Indentation Depth [nm]', 'FontSize', 12, 'FontWeight', 'bold');
ylabel('Load [mN]', 'FontSize', 12, 'FontWeight', 'bold' );
axis([-5 max(X(:))*1.2 0 max(Y(:))*1.2]):
% Fig 2: critical shear stress vs pop-in depth plot --
f2 = figure('Units', 'normalized', 'Position',...
[0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig2);
for i=1:length(array)
  p1 = plot(x_pop(i),y_pop(i),'r*');
h_p1 = get(gca,'Children');
   hold on
end
\label{eq:p2} \begin{array}{l} p2 = plot(xf,yf,'g-'); \\ h_p2 = get(gca,'Children'); \\ hleg_2 = [h_p1(1),h_p2(1)]; \\ legend(hleg_2,'pop in data', 'linear fit','Location','SouthEast'); \end{array}
title (horzcat('Critical Load vs. Extension'),...
'FontSize',10,'FontWeight', 'normal');
xlabel('Extension at Pop-In [nm]');
ylabel('Critical Load [mN]');
grid on
axis([0 max(x_pop)*2 0 max(y_pop)*2]);
% Fig 3: hertzian fitting plot --
f3a = figure('Units', 'normalized', 'Position',...
[0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig3a);
lv = 0;
for i=1:length(array)
p1=plot(Xe(:,i) + lv*x_gap_Fig3, Ye(:,i),'.');
    h_p1 = get(gca,'Children');
   hold on
   p2=plot(Xe(:,i) + lv*5, yf_tip(:,i),'g.');
   h_p2 = get(gca,'Children');
  hold on
lv = lv + 1;
end
h_fig3 = gca;
set(h_fig3, 'LineWidth', 1.5, 'FontWeight', 'normal', 'FontSize', 12);
ab4 = max(Ye(:)) * y_gap_Fig3;
ab5 = max(Xe(:)) + length(array) * x_gap_Fig3;
axis([0 ab5 0 ab4]);
hleg_3 = [h_p1(1); h_p2(1)];
legend(hleg_3,'original data', 'fitting curve')
annotation('textbox', [0.14 0.82 0.3 0.08], 'String',...
   {['av. R = ' num2str(int16(tip_rad_av)) ' +/- '
num2str(int16(tip_rad_std)) 'nm']},...
    'BackGroundColor',[1.0, 1.0, 1.0]);
title (horzcat('Herzian fit of elastic loading part'),...
'FontSize',10,'FontWeight', 'normal');
xlabel('Indentation Depth [nm]');
ylabel('Load [mN]');
xlim([0 60]):
axis([0 50 0 1.6]);
grid on
f3b = figure('Units', 'normalized', 'Position',...
[0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig3b);
lv = 0;
for i=1:length(array)
p1=plot(Xe(:,i).^(3/2), Ye(:,i), '.', 'Color', cm(i,:));
    h_p1 = get(gca,'Children');
   |v = |v + 1|
   hold on
end
xlim([0 150]);
grid on
f3c = figure('Units', 'normalized', 'Position',
   [0.3, 0.3, 0.3*smp, 0.4*smp],'visible',vFig3c);
lv = 0;
for i=1:length(array)
   p1=plot((Xe(:,i)+coef_tip_aux(i)).^(3/2), Ye(:,i), '.', 'Color', cm(i,:));
```

h_p1 = get(gca,'Children');
Iv = Iv + 1;
hold on
end
vlim((0.1501))
and on
giù un
% Fig.4: critical shear stress analysis plot
fa - fauro/! Inite! 'normalized! 'Decition!
14 - Ilgure (onics, nonnaized, rostion,
[0.3, 0.5, 0.5] Silip, 0.4 Silip], VISIDIE ,VFIB4),
where the descent AN
xuar = [1:(iengtn(drtay))];
n 4 - n let (0:0 001 (length (arrest)) + 1 - (//2 to i)   - 1)
$p_4 = prot(0.0.001, tengt(1(a1ray)+1, G/(2 \cdot p_1), t - );$
n_p4 = get(gca, Children );
hold on
p5 = bar(xbar,css./(10 <sup>-9</sup> ));
h_p5 = get(gca, 'Children');
hleg_4 = [h_p4(1); h_p5(1)];
axis([0.5 length(array)+0.5 0 30]);
set(gca, 'XTick', 0:length(array));
set(gca;'XTickLabel',horzcat([0],array));
set(gca,'YGrid','on');
title (horzcat('Critical Shear Stress'),
'FontSize',10,'FontWeight', 'normal');
wi=legend(hleg_4, 'Theoretical Strength (G/2pi)', 'Critical Shear Stress','Location','NorthEast');
xlabel('Indentation Number');
ylabel('Shear Stress [GPa]');
%% directory management
% =====================================
cd(ex_dir);