Extreme elastic deformable ceramics on the nanoscale: Cr$_x$B$_y$O$_z$ nanowire as an example

G Csiszár$^{1,3,*}$, R Lawitzki$^1$ and O Csiszár$^{2,4,5}$

$^1$ Materials Physics Department, University of Stuttgart, Max Planck Institute for Intelligent Systems Campus, Heisenbergstraße 3, 70565 Stuttgart, Germany
$^2$ Faculty of Basic Sciences, University of Applied Sciences Esslingen, Kanalstraße 33, 73728 Esslingen, Germany
$^3$ http://csiszar.web.elte.hu/
$^4$ https://www.hs-esslingen.de/personen/orsolya-csiszar/
$^5$ Also at Institute of Applied Mathematics, Óbuda University, Budapest, Hungary.

* Author to whom any correspondence should be addressed.
E-mail: Gabor.Csiszar@mp.inw.uni-stuttgart.de, Robert.Lawitzki@mp.inw.uni-stuttgart.de and Orsolya.Csiszar@hs-esslingen.de

Keywords: ceramics, non-linear elasticity, packing density, chromium-boron-oxide, second-order elastic constant

Supplementary material for this article is available online

Abstract

Large quantities of chromium-boron-oxide-based nanowires (NWs) were synthesized via electrodeposition. Transmission electron microscopy investigations led to the conclusion that the deposited oxides formed a homogeneously distributed amorphous structure throughout the whole NW. X-ray photoemission spectroscopy analysis revealed that the prevailing constituents as a statistical ensemble are the (super)hard and brittle CrBO$_3$, Cr$_2$O$_3$, Cr, and B$_6$O phases with the majority of CrBO$_3$. The proposed mathematical model utilizing a non-linear geometrical approximation has been found appropriate to characterize the bending behavior of the NWs without any additional mechanical non-linearity in the small-to-moderate regime. The inhomogeneously evolved strain along the NWs at the highest applied force exhibited an enormous relative displacement of 24% at the most strained region, and the 1st Piola-Kirchhoff stresses have turned out to be in the range of about −25 to +10 GPa. Furthermore, the different contributions in the 1st Piola-Kirchhoff stress tensor components indicate that the presence of a prevailing shear effect can significantly modify the resulting axial stresses. The fitted deflection curves propose varying second-order elastic constants. In general, the determined second-order elastic constants, $C_{12}$ and $C_{44}$ are slightly lowered with an increasing external applied load. These values are significantly lower than those in earlier experimental and DFT findings for the 2D-, and 3D counterparts of the constituents. The slight reduction with increasing loading is followed by a considerable drop in the second-order elastic constants with 25%–30% at the largest applied concentrated force. The observed reductive figures may stem from structural disordering in the amorphous phase.

1. Introduction

Nanowires have gained significant research interest as the field of nanotechnology has developed. They have considerable potential in nanotechnology not only from an application, but also from a theoretical point of view due to their unique mechanical, magnetic, and electronic characteristics. For instance, their mechanical behavior considerably differ from their two-(2D) or three-dimensional (3D) counterparts [1–13]. Additionally, based on recent studies, one-dimensional objects may have significantly softer elastic aspects in response to external loads [14, 15] compared to their 2D and 3D counterparts. These unique features may arise from a more relaxed structure due to the influence of the surface, the large surface area to volume ratio, clustering, and the spatial confinement of atoms.
From a compositional perspective, at first sight, the elastic properties of Cr-, or Cr-based systems seem to be well-established based on both theoretical [16] and experimental [17–19] findings. However, in chromium-based alloys and in pure chromium due to the phenomenon of spin-density-wave antiferromagnetic ordering, many physical properties, including elastic properties, can significantly be affected in unclear ways [20]. As key-players of chromium-based systems, chromium oxides are of significant interest due to their diverse technological applications [21]. Previous theoretical interests in these oxides were mainly focused on the transition from an insulator to a semiconductor or a metal [22]. Lately, as one of the most popular candidates for coating of high-temperature materials, Cr₂O₃ has gained increasing scientific interest because of its excellent corrosion-resistant properties [23, 24].

In general, oxide materials have always been found as brittle but relatively strong materials. The strongest materials very often contain oxygen, boron, carbon, and nitrogen, or a composition of these constituents [25]. Frequently, only these lightweight elements are found in hard, or superhard structures or compounds [26]. In these materials, the high bonding strength derives from the small atomic volumes, and the absence of $p$-orbital in the electron core. A promising candidate is the synthetic boron suboxide (BₓO), which has been found as a superhard material after diamond. Hard materials beyond the B-C-N-O systems that consist of metallic components (including transition-metal borides to oxides [27]) have been extensively studied in the last decades. Transition metal borates, in particular, oxyborates MBO₃ have attracted attention due to their diverse magnetic and electrochemical properties. Here, M refers to 3$d$ transition metal ions as Cr, Ti, Fe, V with a calcite mineral structure [28]. Among the compounds with the general formula MBO₃, chromium borate CrBO₃ is the least studied in several respects [29, 30]. However, based on its antiferromagnetic and ceramic property, CrBO₃ has already been applied in atomic force microscopy (AFM) tools, and as a semi-ionic conductor material.

To integrate chromium-boron-oxide-type NWs into nano-/microsystems, an understanding of their mechanical characteristics, also under increasing mechanical/thermal load is important. Furthermore, thorough analyses of ceramic wires via experiments lack; they are drastically less frequently examined than their metallic counterparts.

Regarding the experimental methods, there is a wide variety of testing methods to study the NWs’ mechanical behavior. One of the most popular method is AFM, where the force-displacement relation is determined by recording the force of the AFM tip in contact with the NW. This can be realized by deflecting the nanoscale cantilevers [31] in the so-called ‘three-point’ bending test. This three-point bending method was employed to study the elastic property of several types of NWs such as Nb₂O₅ [32], CuO [33], Si [34], ZnO [35], and Au [36]. Another prolific method is nanoindentation, which provided an alternative method for testing the mechanical behavior of Si [34, 36], Au [36], ZnO [37], and Ag [38, 39] NWs. However, nanoindentation suffers from several inconsistencies, since the theory was developed for thin films (2D) and bulk (3D) materials [40, 41]. Therefore, it can predict a considerable underestimation of the elastic modulus [34]. The elastic/plastic deformation of NWs at the nano-/mesoscale can also be observed in situ by integrating an AFM/nanoindenter into a scanning electron microscope (SEM) or transmission electron microscope (TEM). Micro-/nanomanipulators, as well as AFM cantilevers, have already been implemented with great success in buckling [42, 43], tensile [44, 45], and bending tests [46, 47]. The benefit of applying nano/micro-manipulators is to make possible to investigate single nanowires, and to control the point-load, and therefore, the bending process accurately. Deflection curves can then be investigated theoretically, since the theoretical background of bending, even in the nonlinear regime, is almost straightforward.

This study presents in situ elastostatic bending tests on fabricated chromium-boron-oxide-based NWs conducted in the SEM equipped by a nano-/micromanipulator. We carry out structural-, and accurate chemical analyses using TEM, energy-dispersive x-ray spectroscopy (EDX), x-ray photoelectron spectroscopy (XPS) methods, and analyze SEM images of the bending responses conducted by using the nano-/micromanipulator. Under different applied loads, the deflection curves-, and thus the elastic properties of the NWs are determined in the small-to-moderate elastic regime.

2. Theoretical considerations

2.1. Nonlinear elasticity

Let us denote the the initial configuration at the equilibrium state by

\[ X = (x, y, z). \]

To describe the non-linear behavior of the nanowire-bending in terms of elasticity, we propose the following displacement field (see figure 1):

\[ Y(X) = (u, v, w) = (-z \sin \theta(x) + x \cos \theta(x) - x, 0, z \cos \theta(x) + x \sin \theta(x) - z); \]
i.e. the relationship between \( \{x, y, z\} \) and \( \{u, v, w\} \) is

\[
    u = -z \sin \theta(x) + x \cos \theta(x) - x, \\
    v \equiv 0, \\
    w = z \cos \theta(x) + x \sin \theta(x) - z.
\]

From the proposed displacement field, we can determine the deformation gradient tensor by

\[
    \mathbf{F} = \frac{\partial \mathbf{Y}}{\partial \mathbf{X}}._{ij} i_j.
\]

To take geometrical non-linearity into account, the corresponding Green-Lagrange strain tensor (GL), \( \mathbf{E}_{ij} \), can be derived as

\[
    \mathbf{E} = \frac{1}{2} \left( \mathbf{F}^T \mathbf{F} - \mathbf{I} \right),
\]

where \( \mathbf{I} \) is the unit matrix. In the frame of the proposed \( \mathbf{Y}(\mathbf{X}) \) mapping defined in equations (1)–(3), the non-zero \( \mathbf{E}_{ij} \) components give

\[
    \mathbf{E}_{xx} = \frac{1}{2} \partial_x \theta [(x^2 + z^2) \partial_x \theta - 2z],
\]

and

\[
    \mathbf{E}_{xz} = \mathbf{E}_{zx} = \frac{1}{2} x \partial_x \theta.
\]

By considering a two-dimensional nonlinear isotropic material, the strain energy density depends only on the invariants of the strain tensor, \( \mathbf{E} \) [48]. In the limit of a third-order approximation, the strain energy density, \( \mathcal{W} \), reads

\[
    \mathcal{W}(\mathbf{E}) = \frac{C_{12}}{2} \text{Tr}(\mathbf{E})^2 + C_{44} \text{Tr}(\mathbf{E}^2)
    + \frac{1}{4} (C_{111} - C_{112}) \text{Tr}(\mathbf{E}) \text{Tr}(\mathbf{E}^2)
    + \frac{1}{4} \left( C_{112} - \frac{1}{3} C_{111} \right) \text{Tr}(\mathbf{E}^3),
\]

where \( C_{12} \) and \( C_{44} \) are the second-order elastic constants (SOECs; \( C_{ijkl} = \partial^2 \mathcal{W}/\partial E_{ij} \partial E_{kl} \) at \( \mathbf{E} = 0 \)), and \( C_{111} \) and \( C_{112} \) are the standard third-order elastic constants (TOECs; \( C_{ijklmn} = \partial^3 \mathcal{W}/\partial E_{ij} \partial E_{kl} \partial E_{mn} \) at \( \mathbf{E} = 0 \)) [48] using the (contracted) Voigt notation (\( C_{12}^{\text{Voigt}} = C_{12}^{\text{tensorial}} \), e.g. \( C_{44}^{\text{Voigt}} = C_{44}^{\text{tensorial}} \), \( C_{111}^{\text{Voigt}} = C_{111}^{\text{tensorial}} \), and \( C_{112}^{\text{Voigt}} = C_{112}^{\text{tensorial}} \)). The strain energy density function (see equation (6)) and the calculated GL strain tensor components (see equations (4) and (5)) determine the corresponding second Piola-Kirchhoff stress tensor, \( \mathbf{S} \), where \( \mathbf{S} = \partial \mathcal{W}/\partial \mathbf{E} \). The strain-dependent fourth-order incremental stretch modulus, \( Y_{ijkl} \), can also be determined through the relation of \( 2Y = \partial^2 \mathcal{W}/\partial \mathbf{E}^2 \). Additionally, \( P_{ij} \) the first Piola-Kirchhoff stress tensor can be calculated by utilizing the \( \mathbf{P} = \mathbf{F} \cdot \mathbf{S} \) relation in terms of the \( \mathbf{F} \) and \( \mathbf{S} \) tensors.

The non-zero components of the \( P_{ij} \) stress tensor up to the non-negligible terms (see further details in section 4) read

![Figure 1. Schematic diagram of the geometry of the undeformed- and deformed nanowire in terms of the reference frame [14].](image-url)
The bending moment, defined as $M = \int_A P_{xz} \, dA$ (where $A$ is the beam cross-section), can be calculated by using symmetry considerations:

$$M = \int_A P_{xz} \, dA = -\frac{1}{4} \pi r^4 (C_{12} + 2C_{44}) \partial_x \theta \cos \theta$$

$$+ \frac{1}{16} \pi r^4 (4C_{42} + 8C_{44} + C_{111} - C_{112}) x \partial_x^2 \theta \sin \theta + O(\partial_x^3 \theta).$$

To incorporate the full non-linearity of the curvature, we need to consider the following. By definition, the curvature can be given as a function of the current length element, $s$, as

$$\kappa = \partial_s \theta = \frac{\partial_x^2 \theta w}{(1 + (\partial_x w)^2)^{3/2}} = \partial_s \theta \partial_x x,$$

where $w = w(x)$ represents the deflection as a function of $x$. Since $\partial_x w = \tan \theta$ is considered, $\partial_x s = \frac{1}{\cos \theta}$ and $(\partial_x w)^2 = \frac{1}{\cos^2 \theta} - 1$, thus in the range of $0 < \theta < 90^\circ$, we have

$$\partial_x s = \frac{1}{\cos \theta} = (1 + (\partial_x w)^2)^{1/2}. \quad (13)$$

As a result, equation (11) can be formulated by

$$M = F(L - x) = I(G_{12} + 2C_{44}) \kappa \partial_x s \cos \theta$$

$$- \frac{1}{4} I(4C_{42} + 8C_{44} + C_{111} - C_{112}) x \kappa x \partial_x^2 s \sin \theta + O(\partial_x^3 \theta),$$

where $\int_A dA x^2 = I$ is the second moment of inertia ($r^2 \pi / 4$ for circular cross-section). Note that we follow the positive beam sign convention, where a positive bending moment bends a beam so that the top of the beam is in compression.

To conclude, a complete non-linear geometrical/mechanical description of bending of NWs up to higher orders can be conducted in terms of the bending moment, $M$, the non-zero $E_{ij}$, $P_{ij}$ tensor components, the corresponding $Y_{kin}$ moduli, and experimental deflection curves.
3. Experimental procedure

3.1. Electrodeposition

Porous polycarbonate track-etched membranes with nominal pore sizes of 50 and 100 nm from WHATMAN™ were used to synthesize the NWs of interest. The pores were filled by employing electrodeposition with an aqueous electrolyte consisting of 0.2M CrCl3·6H2O and 0.4M H3BO3. Since the hexa-aqua chromium(III) complex [Cr(H2O)6]3+/2+ is significantly resistant to destabilization, to destabilize the complex, an additional complexing agent, HCOOH, is used. For the complexes to form, the electrolyte is rested for 24 hours before use. Furthermore, a 250 nm thick gold layer serving as a working electrode was sputtered on one side of the membrane. The electrodeposition was conducted in a two-electrode electrochemical cell system in which a Cu plate served as a counter electrode.

For the TEM investigation, the electrodeposition with a nominal pore size of 50 nm was carried out at a potential of \( E = -1 \), 8 V for 2 minutes. After the electrodeposition, the membrane was placed into a 10 ml tube and dissolved in 0.7 ml dichloromethane (CH2Cl2) in an ultrasonic bath at a temperature of 40 °C for 3 minutes. As a following step, 0.1 ml of ethanol was added to CH2Cl2 solution, the wires were pipetted on a nickel TEM grid (with an amorphous carbon film) with a mesh size of 200 μm (Plano).

For the SEM investigation and the bending tests, the electrodeposition was conducted using a membrane with a nominal pore size of 100 nm at a potential of \( E = -1 \), 8 V for 6 minutes. After the deposition, the membrane was dissolved in CH2Cl2 at a temperature of 35 °C for 30 minutes. The produced average length of NWs grown on the sputtered gold layer amounts to about 5–7 μm with an average diameter between 95–105 nm. Additionally, this method was applied to prepare NWs for XPS analysis.

3.2. Characterization

3.2.1. x-ray photoelectron spectroscopy

The composition of the as-prepared a-Cr2O3, CrO3 quasi solid solution was determined by XPS measurements of the Cr 2p1/2, 2p3/2, and O 1s core levels using Thermo Scientific TM Theta Probe Angle-Resolved x-ray Photoelectron Spectrometer System (Theta Probe ARXPS, ThermoFisher). A non-monochromatic twin-gun x-ray source with Al Kα radiation with an operating power of 100 W was applied to stimulate photoemission. The XPS survey spectra were taken with a pass energy of 200 eV. Single peak measurements are done in special scan mode and several pass energies (set by the Avantage software) with a number of frames between 400 and 700 and 1 s measuring time for each frame. All measurements are done using the Flood gun to compensate for the surface charging. The binding energies were calibrated relative to the C 1s binding energy set to 284.8 eV.

3.2.2. Transmission electron microscopy and energy-dispersive x-ray spectroscopy

Single NWs were analyzed on a TEM (CM-200 FEI, Philips, Netherlands) with scanning option operated at 200 kV. The morphology of the NWs was analyzed by bright-field and dark-field imaging. Selected area electron diffraction (SAED) patterns were recorded to check the crystallinity of the NWs. Additionally, the composition of selected NWs was proven with a super ultra-thin window Si detection system by EDAX. Elemental mappings were collected with a probe size of ~3.5 nm, a step size of ~2.5 nm and a dwell time of 10 ms per pixel (resolution 142 eV). The software EDAX Genesis 6.53 was used to evaluate the EDX spectra (by standardless analysis with Cliff–Lorimer thin film approximation and theoretical K factors according to Zaluzec) and for constructing spatial element distribution maps (see figures 2(e), (f)). For improved statistics, the EDX spectra of 3 × 3 pixels have been averaged resulting in ~180 counts/pixel.

3.2.3. SEM equipped with a micromanipulator

Mechanical testing was performed inside an SEM (Quanta 250, FEI, Netherlands) with an acceleration voltage of 30 kV using an MM3A-EM micromanipulator (Kleindiek Nanotechnik, Germany) equipped with an FMS-EM force readout tool and an FMT-120 B force sensor. A dual-beam focused ion beam-scanning electron microscope, FIB-SEM, (SCIOS, FEI, Netherlands) was used to transfer single NWs onto pre-fabricated (via electrochemical polishing in NaOH) tungsten posts and fix them in place by Pt-deposition. The horizontally placed NWs in the SEM were deflected by exerting an external force at the free end while keeping the NW in the same horizontal plane. Each nanowire was elastically deformed multiple times with increasing applied force. Finally, SEM images of the bending responses under different applied loads were analyzed to determine the deflection point-by-point by utilizing a skeletonization algorithm implemented in the ImageJ software.
4. Results

4.1. Morphology and composition analysis by using TEM, EDX and XPS

The morphology and composition of the NWs were analyzed by TEM. A bright-field image of a typical NW is shown in figure 2(a). The ‘drops’ around the presented NW are residuals from the polycarbonate membrane. The average length after analysis of several NWs (more than a 100 in bunches, and around 20 separately situated; also determined via SEM) was found to be between 6 to 7 μm, and the diameter is about (100 ± 5) nm. The contrast of the NW shown in the bright and dark field images (figures 2(c), (d)) is rather homogeneous; no individual grains can be identified. This is further supported by the diffuse rings and absence of spots in the diffraction pattern in figure 2(b), proving an amorphous structure of the NW (note here that the residuals of the polycarbonate membrane and the carbon film on the grid may also contribute to the diffuse scattering). The radii of the two diffuse rings in figure 2(b) correspond to distances of 2.1 and 1.3 Å. These are very close to the nearest neighbor distances of Cr-O (1.996 Å) and B-O (1.372 Å) in CrBO3 [49]. Furthermore, the composition of the wires was also studied by TEM EDX. As shown in the elemental maps in figures 2(e) and (f), the NW consists of Cr and O (note here that the element of B is also a constituent as will be investigated later through XPS analysis; the analysis of the low energy B K-line provided by EDX would be ‘highly speculative’ and thus not considered here). The oxygen content is homogeneously distributed within the wires, and a core–shell structure can be excluded. It has to be mentioned here that due the vicinity of the EDX spectra of the Cr L-lines (~573 eV) and the O K-line (~525 eV), a differentiation of the O and the Cr EDX signal, and consequently, an accurate elemental quantification is not feasible. Regarding the colored EDX maps in figure 2, the peak corresponding to the superposition of the Cr L-line and the O K-line was set to solely the O intensity and the Cr K-line was set to visualize the intensity of the Cr signal (for more details about EDS data analysis, the readers may refer to the spectral intensity distribution given in the Electronic Supplementary Information stacks.iop.org/NANOX/2/040001/mmedia). As a consequence, oxygen rich regions (if present) appear with a higher net intensity of the (Cr L + O K) peak with respect to the Cr K peak within the resolution of our EDX map. For the benefit of higher accuracy in detection of the low energy elements, additional XPS measurements were performed leading to a better understanding of the chemical nature of the NWs.

An excerpt of the XPS spectrum covering a range in binding energies from 570 eV to 595 eV is shown in figure 3(a). In this energy range, the two spin-orbit doublet peaks of Cr 2p1/2 and Cr 2p3/2 can be detected. Each of the peaks can be identified as a superposition of several separate signals stemming from Cr, CrBO3, and Cr2O3 (cf table 1). In accordance with the literature (NIST database [50]), the peaks at the Cr 2p1/2-related energies feature a less asymmetric intensity distribution by having three intensity subprofiles superimposed to each other (Cr, Cr2O3, and CrBO3). At the Cr 2p3/2-related energies, the peaks feature a more asymmetric intensity distribution by having the two, main intensity subprofiles as the Cr and CrBO3, and several (undefined) superimposed peaks related to the Cr2O3 phase. The prevailing oxide phases can also be confirmed by the XPS spectra in the analysis of the O 1s line, shown in figure 3(b). This analysis indicates a superposition of three oxide species as the Cr2O3, the CrBO3, and the B4O with a dominating CrBO3 oxide phase (cf table 1).

From a quantitative perspective, based on the findings about the prevailing phases, the integrated regions under the constitutive peaks indicate their relative volume fractions. Considering the integrated peaks in the analysis of the O 1s, and the Cr 2p3/2 lines, the calculated relative volume fractions of the phases CrBO3, Cr2O3, Cr, and B4O are about 0.49:0.21:0.15:0.15, respectively. Note here that the amount of residuals from the
polycarbonate membrane is rather small and therefore can be neglected in the XPS spectra. Hence, an accurate fit can be obtained without considering additional C-O bonds.

To bring this section to a conclusion, the NWs are of amorphous structure with a mixture of metallic Cr and the dominating CrBO₃, Cr₂O₃, and B₆O oxide phases that homogeneously distributed throughout the entire volume of NWs.

4.2. Mechanical bending.

For the determination of the deflection curves, \( w(x) \), concentrated lateral forces were exerted at the free end. While the clamped end connected to the W-post was stable, a force measurement tip was moved in a direction perpendicular (in the reference frame) to the NW to employ gradually increasing lateral force. Furthermore, during bending, the initial position of the contacting tip slipped on the surface of the NW as well-visualized in figure 4. Figures 4(a)–(d) illustrate a series of snapshots of SEM images that display the process of bending of a typical individual NW with effective lengths of 3.671 ± 0.02, 3.476 ± 0.02, 3.193 ± 0.02, and 2.644 ± 0.02 μm, and a radius of 83 ± 6 nm. For the sake of the evaluation, a Cartesian coordinate system is given in such a way, where the origin is defined as the point where the nanowire contacts the W post, whereas the 'ending point', where the manipulator touches the NW (see illustration in figure 4(a)). As a consequence, the effective length is the distance between the origin and the ending point along the NW. As a preprocessing operation, a skeletonization algorithm was applied using the distance transformation procedure implemented in the ImageJ software. Using this method, the highest accuracy in determining the deflection paths is achieved (denoted as the middle line in figure 4(a)). As demonstrated in figures 4(a)–(d), the increasing deflection indicates the gradually increased lateral force within the range of 537 ± 35 to 940 ± 20 nN. At higher applied forces, residual deformation was detected which is out of the current study’s scope. After each bending test, the tip was unloaded, and the entire NW moved back to its initial position and utterly restored its original shape.

| Species   | Photo-electron line | Lit. [eV] | Meas. [eV] | Peak Area [Cps.eV] |
|-----------|---------------------|-----------|------------|-------------------|
| Cr        | Cr 2p₁/₂            | 583.5     | 583.77     | 50                |
| Cr₂O₃     | Cr 2p₁/₂            | 586.2     | 586.87     | 65                |
| CrBO₃     | Cr 2p₁/₂            | 577.9     | 577.27     | (undefined)       |
| Cr₂O₃     | O 1s                | 532.20    | 532.24     | 150               |
| CrBO₃     | O 1s                | 530.80    | 530.83     | 60                |
| B₆O       | O 1s                | 533.67    | 533.68     | 50                |

Figure 3. XPS spectra of the chromium-boron-oxide NWs showing (a) the two spinorbit doublet peaks of Cr 2p₁/₂ and Cr 2p₃/₄. Each peak in the spectra is a superposition of at least two of the species Cr, Cr₂O₃, and CrBO₃ as indicated accordingly; (b) spectra of the three separate peaks of the O 1s line referring to different types of oxides as B₆O, Cr₂O₃, and the dominating CrBO₃.
As shown in figure 5, the maximum displacement, referred to the effective length, reaches about 1500 nm at the lowest applied force, and 1750 nm at 940 nN with an effective length of 2.644 μm. The deflection at 940 nN causes a deformation still in the elastic regime. To capture the nonlinear effects in solids, color-coded deflection curves, $w(x)$ (dashed line), are determined by solving equation (14) numerically using the shooting method. The numerical fitting procedure was carried out by solving equation (14) with different $C_{ij}$ and $C_{klm}$ constant values. Taking into account that the DE is sensitive to the parameters given, we applied different ranges in the parameter space of $C_{ij}$ and $C_{klm}$, and minimized the least square error between the predicted and the experimental result. The numerical solutions confirm in the entire range of the experimental data that the proposed model within 5% experimental error may provide an appropriate physical description for deflection in the small-to-moderate regime. Examining the fitted theoretical curves, at small applied force, the curvature along the wire can be approximated by a constant ($\approx 1/R$); however, at larger applied forces, the curvature deviates from a constant behavior. As expected, towards the free end of the NW, the curvature converges to infinity; consequently, the bending effect vanishes.

As a result of the numerical fitting procedure, we found that the terms in equation (14) consisting of quadratic or higher-order terms concerning the curvature, contribute to the overall momentum only at steeper tangents of the bending curve (even larger applied forces than employed in the experimental study). Consequently, the quadratic geometrical approximation without any additional mechanical non-linearity (usage of $C_{klm}$) is found to be sufficient in respect to the small-to-moderate regime at all the applied forces as shown by the fitted color-coded deflection curves in figure 5. Thus, the generated deflections, in the small-to-moderate regime, cannot provide insights about the TOECs of an amorphous structure within experimental error.

---

**Figure 4.** (a)–(d) A series of SEM snapshots of a typical Cr$_x$B$_y$O$_z$ NW exerted by lateral forces. The applied forces are also given at the different stages of deflection. Schematic diagram of a Cartesian-coordinate system depicted in (a) demonstrates the applied method used to determine the deflection curves denoted as the middle line. The dotted line represents the experimental data points within an error of about 7 nm in the entire range. The scale bar given in (b) holds also for all images in the series.

**Figure 5.** Typical deflection paths determined by displacements at points along the middle lines with an average distance of about 100 nm as a result of the applied forces ranging from (a) 537 nN to (d) 940 nN. Additionally, deflection curves defined implicitly in the nonlinear theoretical moment function (see section 2) are shown by color-coded dashed lines after fitting numerically to the experimental data. The experimental error is in the order of the size of the symbols.
The results with respect to the SOECs after the applied numerical procedure is tabulated in table 2. The determined SOECs based on the current theory and experiments indicate significantly lower material properties. Figures compared to previous findings for chromium (see table 3) confirm this suggested by DFT calculations, and experiments. In the case of Cr$_2$O$_3$, the corresponding figures provide a considerably higher value for both elastic constants due to the existence of covalent bonds. Regarding the CrBO$_3$ phase, the corresponding values reported in an earlier study also indicate a stiffer material behavior. Lastly, the super-hard material, boron suboxide, B$_6$O, implies an even stiffer elastic response behavior in a bending test. On the contrary, the values in a table 3, in the field of metallic, semiconducting, ceramic, amorphous, and crystalline NWs, the oxide type of NWs irrespective to having translational symmetry, and some metallic elements as Ni, Pt, Cu indicate a significant reduction in SOECs, or in Young’s modulus compared to their bulk counterparts (the only exception

| Constituent | Method | $C_{12}$ | $C_{44}$ | $C_{11}$ |
|-------------|--------|----------|----------|----------|
| Cr          | DFT    | 73 [52], 93 [53] | 119 [52], 103 [53] | 311,299 |
| Cr$_2$O$_3$ | Exp.   | 91 [17] | 103 [17] | 297     |
| CrBO$_3$    | DFT    | 160 [54] | 160 [54] | 480     |
| B$_6$O      | DFT    | 132 [55] | 104 [55] | 340     |
|              |        | 140 [56] | 180 [56] | 500     |

* The effective length of the nanowire.

| Constituent | Method | $E$ or $C_{11}$ | $E_{bulk}$ or $C_{11}^{bulk}$ | Temperature [K] |
|-------------|--------|----------------|--------------------------------|-----------------|
| Si, crystalline | Exp. | 95–210 (E) [57] | 112 [58] | 300 |
| Si, crystalline | MD | 171 (E) [59] | — | 300 |
| Ge, crystalline | Exp. | 112–160 (E) [57] | 80 [58] | 300 |
| ZnO, crystalline | Exp. | 133 (E) [60] | 145 [61] | 300 |
| Ni, crystalline | MD | 291 (E) [62] | 220 [58] | 3100 |
| Ni$_2$O$_3$, crystalline | MD | 134 (E) [63] | — | 1800 |
| Ni, crystalline | MD | 136 (E) [64] | — | 300 |
| Au, crystalline | MD | 116 (E) [65] | 78 [58] | 2–600 |
| Au, crystalline | MD | 55–81 [66], 55 [64] (E) | — | 300 |
| Pt, amorphous | Exp. | 110–170 (C$_{11}$) [14] | 347 [58] | 300 |
| Pt, crystalline | MD | 109157 (E) [66] | 170 [58] | 300 |
| Cu, crystalline | MD | 80 [64], 85 [67] (E) | 128 [58] | 300 |
| Cu, polycrystalline | Exp. | 67–78 (C$_{11}$) [15] | 169 [58] | 300 |
| Ag, crystalline | MD | 80 (E) [68] | 80 [58] | 300 |
| Al$_2$O$_3$, amorphous | Exp. | 110–120 (E) [69] | 344 [70] | 300 |
| SiO$_2$, amorphous | MD | 40(E) [59] | 65 [71] | 300 |
| Nb$_2$O$_5$, crystalline | Exp. | 65 (E) [69] | 134 [72] | 300 |
| FeO$_x$-Fe composite, polycryst. | Exp. | 250–350 (C$_{11}$) [14] | 250–350 (E$_{bulk}$) [73] | 300 |
| Fe$_2$O$_3$-Fe composite, polycryst. | Exp. | 235–240 (C$_{11}$) [14] | 250–350 (E$_{bulk}$) [73] | 300 |

* SOECs are given in GPa.
* $E$ and $C_{11}$ are given in GPa.
* Diameter is larger than 15 nm.
is the ZnO, where the reduction is less considerable). The reduction is nearly negligible in the case of Au and Ag, however, they also show a reduction compared to the bulk aspects. On the contrary, in the case of Si and Ge, the corresponding elastic constants increase significantly. Note here that the listed values can also depend on the geometry and dimensions of the NW. In this study, the significant reduction of the elastic constants is also confirmed for the chromium-boron-oxide composite NWs. Consequently, it could be said that the oxide type of materials, as well as the metallic counterparts behave elastically softer compared to their bulk in a nonlinear deformation process on the nanoscale.

5. Discussion

The attention can now be turned to the calculated non-linear strain, stress, and the incremental stretch moduli. The non-zero evolving strains can be plotted as a function of the NW-length (see figure 6). Here, the physical parameters, \( C_{ij} \) are determined by solving the differential equation given in equation (14).

In figure 6, the \( E_{zx} \) axial strain develops during bending emphasizing that this vanishing strain at the free end of the NW contributes significantly to the overall deformation between the clamped- and free ends. At \( z = 0 \) (black line), the middle line suffers from a considerable 4% strain at the most strained region (\( F = 537 \) nN), which is well above the elastic limit of any kind of chromium-(boron)-oxide-based, or superhard material. At the highest applied force, the axial strain reaches 14% at the most tensed region. The \( E_{zx} = E_{zz} \) strains also significantly exceed the bulk elastic limit with values about −15%, and −24%, being still in the elastic regime. This negative (reversed) shear strain has also been found in an earlier study for boron-epoxy amorphous composite in the case when the angle, \( \alpha \), between the external applied force and the cylindrical axial direction falls into the range of \( \pi/3 < \alpha < \pi/2 \) [74].

The corresponding stress tensor components (\( P_{xx}, P_{xz}, P_{zx}, \) and \( P_{zz} \)) all suggest rather high stress evolved along the NW. In the case of \( P_{xx} \), the stress fluctuates between +3 and −3 GPa (\( F = 537 \) nN), while this physical parameter indicates a range of +4.5−6.5 GPa with 940 nN. Similarly, the determined ranges for \( P_{xz}, P_{zx} \), and \( P_{zz} \) equate to 0−10(537 nN)/0−7.2(940 nN) GPa, 0−18(537 nN)/0−25(940 nN) GPa, and 0−12(537 nN)/0−18(940 nN) GPa, respectively. Note that as mentioned in section 4.2, the TOECs cannot be determined and therefore the terms consisting \( C_{111} \) and \( C_{112} \) in equations (7)−(10) are not taken into account.

The proposed model may be limited to particular deformations where the transverse deformation is negligible with a corresponding Poisson ratio, \( \nu \ll 0.3 \). As shown in figure 6, the \( E_{zx} \) values are mostly positive, whereas the corresponding \( P_{xx} \) values show a different behavior. This is because \( P_{xx} \) can be calculated as a sum of terms containing components of the deformation gradient, and the 2nd Piola-Kirchhoff tensors: \( P_{xx} = F_{xx} S_{xx} + F_{xx} S_{xx} \). Note that the shear strain comes into play when the respective stress and \( F_{xx} \) are both non-negligible. In the inset of figure 7(b), the different contributions of the additive terms in \( P_{xx} \) are visualized, indicating that the presence of a significant shear effect can modify the resulting axial stress. This phenomenon has also been found in an earlier study [75], where the evolved pure shear deformation induced a significant increase in the total elongation. The \( P_{xx} \) and \( P_{zx} \) components suggest a similar behavior. The dissimilarity derives from the fact that the \( P_{xz} = F_{xz} S_{xz} \), whereas \( P_{zx} = F_{xz} S_{xz} + F_{xz} S_{xz} \). These two rather different measures are reflected in the much larger stress values of the \( P_{xz} \). In figure 7(e), the \( P_{zz} = F_{xz} S_{xz} \) tensor component is plotted emphasizing its non-zero nature.

The incremental stretch moduli, \( 2Y_{ijkl} = \partial S_{ij}/\partial E_{kl} \) as a function of the SOECs can be determined in the frame of nonlinear geometrical approximation. Considering the symmetries in \( S_{ij} \) and \( E_{kl} \), only the non-zero
component plays a role. Note that the weighted average of the constitutive SOECs would imply a significantly different elastic behavior from those determined experimentally (compare tables 3 and 2). The NWs as 1D objects indicate a significantly softer material response behavior than the 2D-, or 3D counterparts. Additionally, this softer behavior becomes even softer in the course of a considerable elastic strain evolution during bending.

5.1. Strain-induced structural changes

The elastic behavior of amorphous composites may be closely related to the degree of disorder, which can be discussed in terms of the atomic packing density [76–78]. Here, we propose a possible mechanism for structural changes during elastostatic bending by applying short-range order (SRO) atomic clusters at room temperature (RT). The proposed mechanism is based on previous findings for amorphous, metallic alloys. Elastic deformation of amorphous materials below yield point (at RT) is most probably caused by structural disordering. As a previous study revealed, Young’s modulus resulted in a dramatic rise with an increasing packing density [79]. Additionally, disordering and the rate of disordering in an elasto-plastic deformation process depend significantly on the packing density of the amorphous structure. The rate of disordering has been found non-linearly increasing as the packing density increases [79]. Based on these findings, we assume that the chromium-boron-oxide-based amorphous structure in this study has similar features and behaves similarly.

The packing structure can be characterized by the relative fractions of the SRO clusters. Amorphous alloys tend to initially contain the highest fraction of (0,0,12,0)-type polyhedra [79], This suggests an icosahedral order with the densest packing structure and the highest resistance to strain [80]. Furthermore, it has been found that with higher packing density, a higher relative ratio of the icosahedral order was determined. Therefore, we assume that our initial chromium-boron-oxide-based amorphous composite has a similarly high fraction of (0,0,12,0)-type polyhedra. In an elastostatic deformation process, the general principles of the evolution of SRO structures with different initial packing densities has already been investigated [79]. It turned out that fractions of the densely packed polyhedra, such as (0,0,12,0) and (0,1,10,2), decrease with increasing strain, while the fractions of the loosely packed polyhedra, such as (0,3,6,4), increase. The degree of disorder has changed considerably with higher packing density. Furthermore, the rate of change of the relative ratios among the different polyhedron types depends significantly on the packing density. The more densely packed structure has significantly higher disordering rates than a less densely packed one. Consequently, during a highly-strained deformation process, it may happen that the structure changes from a densely packed SRO polyhedra structure to a more loosely packed bunch of clusters. Furthermore, an abrupt change in the elastic response may not be ruled out either.

Thus, as reported in section 4.2, the determined SOECs in terms of the exerted external load may indicate a transition (reversible) featured by a significant reduction in the SOECs. In the course of the elastostatic bending,

\[ Y_{xxxx} = \frac{1}{2}(C_{12} + 2C_{44}) \]
the increased disorder is associated with an increase of the excess free volume (average interatomic spacing), resulting in lowering the atomic bonding force, consequently, lowering the SOECs of the bent NWs. However, the lowering SOECs is strain-dependent, after unloading, the sample regains its initial material property. This phenomenon is well-visualized in cases featured by increasing applied external forces.

To conclude, the observed one order of magnitude higher strain, and the corresponding high stresses may open the doors to new opportunities in various nanoscale applications. However, the physical reasons for the lower initial SOECs values have not yet been fully established.

6. Conclusions

The synthesis of large quantities of chromium-boron-oxide-based NWs was achieved through electrodeposition at RT. The synthesized NWs had an average length between 5–7 μm with diameters ranging between 95–105 nm.

I. The investigation via TEM and EDX led to the conclusion that the deposited oxides formed a homogeneously distributed amorphous structure throughout the whole NW. XPS analysis revealed that the prevailing constituents are the CrBO₃, Cr₂O₃, Cr, and B₆O phases with a majority of the CrBO₃ phase. These components have usually been treated as hard and in the case of B₆O, superhard materials with considerable brittleness.

II. As a result of the theoretical considerations, the nonlinear geometrical approximation has been found sufficient to characterize the bending behavior without any additional mechanical non-linearity in the small-to-moderate regime.

III. The inhomogeneously evolved strain along the NWs at the highest applied force (F=940 nN) exhibits a considerably large relative displacement of about 24% at the most strained region. This emphasizes that the elastic regime is more than an order of magnitude broader compared to that of the 2D-, or 3D counterparts of the constituents. Additionally, the determined non-linear stresses have turned out to be in the range of about −25 to +10 GPa. Furthermore, the different contributions of the additive terms in the axial stress, $P_{xx}$, indicate that the presence of a significant shear effect can modify the resulting axial stress.

IV. In general, the determined $C_{12}$, and $C_{44}$ SOECs are slightly lowered with increasing applied load. These SOECs are significantly lower compared to that of earlier experimental and DFT findings for the 2D-, and 3D counterparts of the constituents. The initial slight reduction with increasing loading is followed by a considerable drop with an amount of 25%–30% at the largest applied concentrated force.

V. The observed reductive behavior of the SOECs may result from structural disordering through reducing fractions of the densely packed polyhedra, while the fractions of the loosely packed polyhedra, increase with increasing strain. Consequently, the increased disorder is associated with an increase in the average interatomic spacing, inducing a lowering of the atomic bonding force, and a lowering of the SOECs.

Acknowledgments

We acknowledge the support of P Schützendübe for providing accurate XPS measurements.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

G Csiszár https://orcid.org/0000-0001-8367-2870
R Lawitzki https://orcid.org/0000-0001-7802-0237
O Csiszár https://orcid.org/0000-0003-1907-1901

References

[1] Csiszár G, Balogh L, Misra A, Zhang X and Ungár T 2011 J. Appl. Phys. 110 043502
[2] Csiszár G 2014 Materials Science and Engineering A 609 185
[70] Shackelford J F, Han Y H, Kim S and Kwon S H 2015 CRC Materials Science and Engineering Handbook (USA: CRC Press) 9781482216530
[71] Han L and Vlassak J 2009 J. Mater. Res. 24 1114
[72] Shcherbina O B, Palatnikov M N and Efremov V V 2012 Inorg. Mater. 48 433
[73] Ouglova A, Berthaud Y, Francois M and Foct F 2006 Corros. Sci. 48 3988
[74] Tsai S W 1966 Technical Report, AFML-TR-66-149 ADA306263 48 Defense Technical Information Center
[75] Matsutani R, Nakada N and Onaka S 2020 Metals 10 654
[76] Albano F, Lacevic N, Falk M L and Glotzer S-C 2004 Materials Science and Engineering A 375 671
[77] Park K-W, Jang J-I, Wakeda M, Shibutani Y and Lee J-C 2007 Scr. Mater. 57 895
[78] Lee J C, Park K W, Kim K H, Fleury E, Lee B J, Wakeda M and Shibutani Y 2007 J. Mater. Res. 22 3087
[79] Park K-W, Lee C-M, Wakeda M, Shibutani Y, Falk M and Lee J-C 2008 Acta Mater. 56 5440
[80] Wakeda M, Shibutani Y, Ogata S and Park J 2007 Intermetallics 15 139