Elasticity and Strength of Nano-Fiber Reinforced Composites from First Principles

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Abstract
Calculations of elastic moduli and theoretical tensile strength of unidirectional composite having continuous nano-fiber reinforcements are performed using ab initio method. Results for tungsten nano-fibers in vanadium matrix are presented as a particular example of the analysis. The dependence of the computed composite elastic moduli on the atomic concentration of W (nearly corresponding to the volume fraction of fibers) is compared with the rule of mixture for an ideal composite. Results show that validity of the linear mixture rule is theoretically justified for most of them. On the other hand, computed values of theoretical strength exhibit a higher monotonous increase only up to about 60% of W and predict a synergy effect. The related analysis based on a creation of internal stresses at the fibre/matrix interface reveals that, in this way, the synergy effect can be explained only partially.

1. Introduction

Ab initio calculations provide a very effective tool for studying materials at atomistic level. Owing to their independence on experimental data (no need for calibration) they can be used also for designing new materials with required parameters. Composites represent one of widely used successful ways to improve mechanical properties of materials, in particular their elastic moduli, strength and fracture toughness. Resulting properties in real engineering macro-composites are functions of many parameters depending on particular design and production technology. However, the situation is not so much complicated for all mechanical properties. For example, the Young modulus of long-fiber composites in the fiber direction can be sufficiently precisely assessed according to a simple linear mixture rule. The previous studies on W-Nb [1] and Mo-V [2] nanocomposite models exhibiting a perfect cohesion on the fibre/matrix interface revealed that the linear mixture rules are valid at the atomistic level e.g. for values of the equilibrium volume and the bulk moduli. In case of the theoretical strength, however, the obtained relationships predicted a synergy behavior in the range of 60-90% of reinforcement fibers.

In the present paper, the elastic moduli and theoretical strength under uniaxial loading of ideal nano-composites of vanadium matrix and long tungsten fibers are computed for different thickness of nano-fibers (from a single atom to several atomic distances). The main aim of this work is to verify the validity of empirical rules of mixture for elastic moduli and, in particular, to asses a possible role of internal stresses in the synergy behavior predicted in case of theoretical tensile strength.

2. Computational details

A model of the nano-composite is built as a periodic repeating of 4x4x1 bcc-based super-cell displayed in Fig. 1.

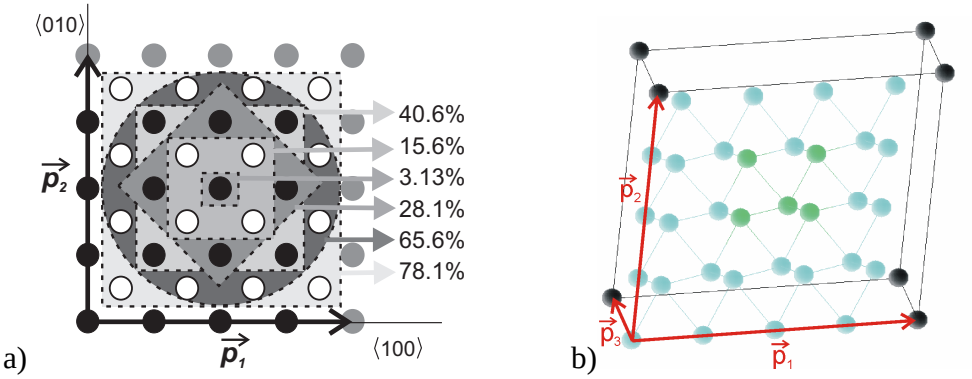

Figure 1: A sample of nano-composite: a) the super-cell model and b) slab containing one W wire that corresponds to 15.6% W concentration.

The crystal basis of our super-cell contains 32 atoms in both A (solid circles) and B (open circles) (001) planes. The grey solid circles belong to other (adjacent) super-cells. The dashed contours define considered interfaces between tungsten (W) wire and vanadium (V) matrix in investigated lamina models of different atomic concentration of W. In order to get few more different concentrations, the V wires in W matrix were also studied. Tungsten concentrations of 59.4%, 71.9% and 84.4% were obtained this way.

Calculation procedure starts by finding the super-cell ground-state. Computation of the total energy E_{tot} per atom as a function of the atomic volume V was applied for this purpose. In order to minimize the interfacial stresses, the atomic positions within the super-cell were relaxed at any volume. Once the minimum of the $E_{tot}(V)$ dependence was found and the equilibrium volume V_0 and the bulk modulus B were obtained, the crystal was subjected to incremental uniaxial elongation in [001] direction. In order to take the Poisson contraction into account, the transverse stresses were relaxed by varying of cell edges (lengths of the translation vectors $\boldsymbol{p_1}$ and $\boldsymbol{p_2}$ in Fig. 1). Using this procedure, the uniaxial loading of composite was simulated in direction parallel to the lamina fibers. Because of high computational demands of such task, the relative atomic positions within the cell were kept constant (as they were obtained for the ground-state).

The dependence of total energy on the relative elongation ε yields the uniaxial stress σ applied on the system as well as the Young modulus E_{001} value. If no other instability precedes, the uniaxial stress σ_{ip} reaches its maximum at the point of inflection on $E_{tot}(\varepsilon)$ function. In such case, the σ_{ip} can be considered to be the theoretical strength of nanocomposite under the conditions of uniaxial loading.

For the electronic structure calculations, we utilized the Vienna Ab initio Simulation Package (VASP) [3]. This code uses projector augmented-wave potential and plane wave basis set. Cut-off energy for the basis set was 290 eV. The exchange-correlation energy was evaluated using the generalized-gradient approximation of Perdew and Wang [4]. 3x3x12 *k*-points mesh was used in all our calculations. The solution was considered to be self-consistent when the energy difference of two consequent iterations was smaller than 0.1 meV. Atomic positions within the super-cell were relaxed using Hellman-Feynman stress tensor.

3. Results

In order to verify reliability of the applied computational procedure, the equilibrium lattice parameter a_0, the bulk modulus B, the Young modulus E_{001} and the Poisson ratio ν were calculated for pure tungsten and pure vanadium using the same super-cell as described in the previous section. The obtained values are listed in Table 1 along with available experimental data. The experimental values of a_0 and B were taken from Ref. [5] and E_{001} values were computed from elastic moduli [6].

Table 1: Computed and experimental values of the equilibrium lattice parameter a_0, the bulk modulus B, the Young modulus E_{001} and Poisson ratio ν for pure W and pure V.

Element		a_0 [nm]	B [GPa]	E_{001} [GPa]	ν
V	calc.	0.298	189	199	0.32
	expt.	0.303	157	151	0.34
W	calc.	0.318	311	389	0.29
	expt.	0.316	313	417	0.28

The agreement of computed and experimental a_0 values is within 2% which is acceptable. The agreement in case of elastic moduli and Poisson ratio for tungsten is also very good (mostly within 5%). Computed elastic moduli for vanadium overestimate those observed experimentally.

Values of the bulk and Young moduli are plotted as functions of the atomic concentration of W in Fig. 2. As the atomic concentration is approximately equal to the volume fraction of fibers V_f, the data points seem to follow the simple linear mixture rule

$$B = \eta V_f B_f + (1 - V_f) E_m, \qquad \text{(Eq. 1)}$$

where B_f and B_m are the bulk moduli of the fiber and matrix, respectively, and η is a factor depending on the cohesion strength between the fiber and the matrix [7].

In case of ideal cohesion η = 1 has to be assumed. The dashed line follows Eq. (1) for experimental values B_f = 270 GPa, B_m = 157 GPa and η = 1. Computed E_{001} values also seem to more or less follow Eq. (1) when the Young's moluli E_f = 417 GPa and E_m = 151 GPa are used instead of B (the dotted line in Fig. 4). Thus, our atomistic results suggest that deviations from Eq. (1) observed for real composites are caused by their imperfections, particularly by reduced interface cohesion.

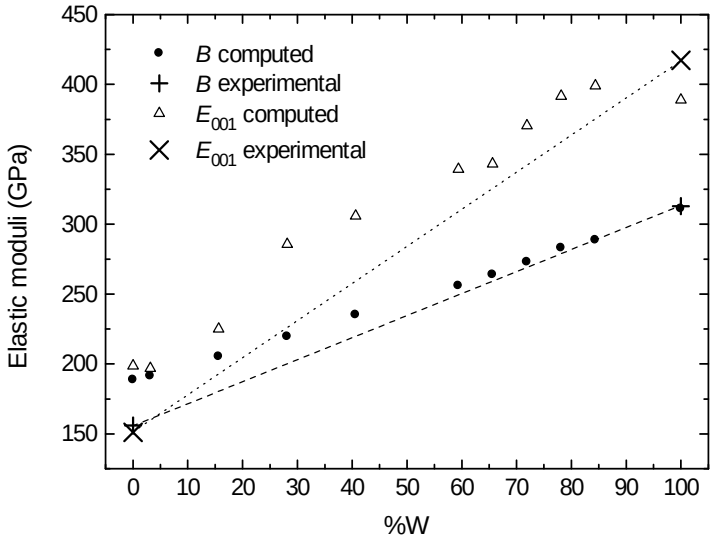

Figure 2: Dependence of the bulk modulus B (circles) and Young molulus E_{001} (triangles) on atomic concentration of tungsten.

Computed values of uniaxial stress σ_{ip} at the point of inflection on the $E_{tot}(\varepsilon)$ curve for pure V and W are listed in Tab. 2 together with available literature data [8, 9]. The correspondence between the data is very good.

Table 2: Computed stresses and strains at inflection points of the $E_{tot}(\varepsilon)$ functions.

Element		σ_{ip} [GPa]	ε_{ip}
V	present work	19.2	0.17
	Ref. [8]	19.8	0.22
W	present work	28.8	0.14
	Ref. [8]	28.9	0.16
	Ref. [9]	28.9	0.12

Fig. 3 displays the σ_{ip} values for all investigated composites (the solid circles). They exhibit simple increasing dependence on atomic concentration of W up to about 60%. Above this concentration they seem to reach even higher value then that of a pure W. It indicates a presence of certain synergy effect between the fiber and the matrix.

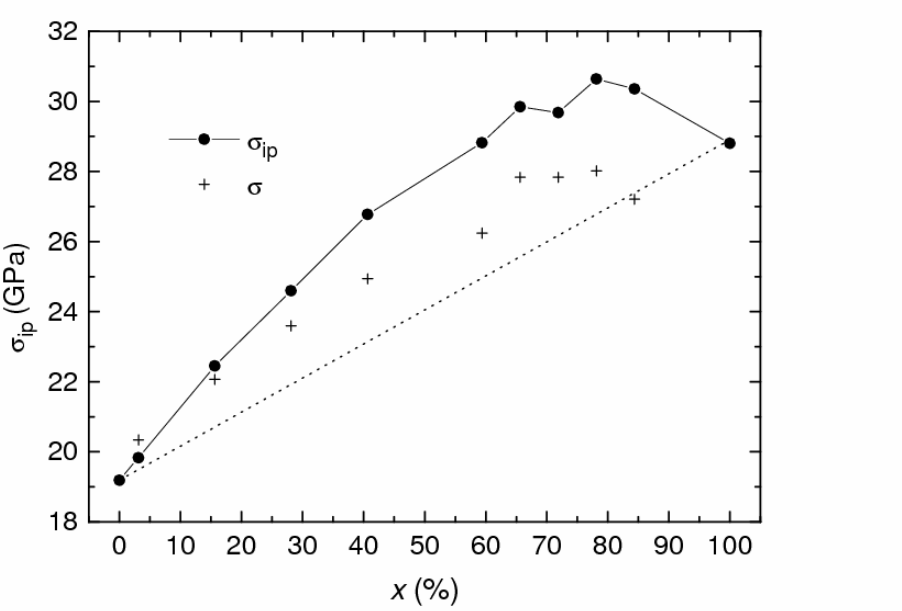

Figure 3: Stress at the inflection point as a function of tungsten concentration *x*.

4. Discussion

This very interesting result is worth subjecting to further study. A possible explanation can be the fact that, due to the lattice mismatch, fibers are under transversal tensile or compressive stresses that can influence the stress-strain response and, thus, the uniaxial tensile strength of the whole composite. Therefore, the stress coupling effect has been also recently studied from first principles [8]. It was observed that, in case of cubic metals, the tensile strength (also evaluated as the maximum tensile stress) increases under the conditions of superimposed tensile transverse stresses. Therefore, a simple model has been developed to verify this theory. The model compares the obtained results for nanocomposites with predictions obtained for two independent ideal crystals of pure W and V. In order to include the stress coupling effect, the individual crystals were loaded in a triaxial mode that mimics the stress state experienced by the fiber or matrix in the composite.

The tensile stress acting on the composite can be evaluated from the relation

$$\sigma = \sigma_f \frac{S_f}{S} + \sigma_m \frac{S_m}{S}, \qquad \text{(Eq. 2)}$$

where σ_f and σ_m represent the tensile stresses acting on fiber and matrix, respectively. Dividing the area S of composite cross-section (see Fig. 1) to the fiber area S_f and the matrix area S_m is the most disputable point of this analysis. According to the computational procedure that was used in the present nanocomposite analysis, the fiber volume fraction as well as the corresponding

ratio $\lambda = \sqrt{S_f / S}$ is constant during the uniaxial loading. Therefore, the ratios λ for each composite model were taken from ground-state lattice parameters. The lattice parameter c_0 (length of the translational vector p_3) of individual crystals of W and V was set equal to that of the composite and the corresponding transverse parameters a_0 (lengths of p_1 and p_2 vectors) were found by relaxation of transverse stresses. The λ ratio was then calculated from a ratio of obtained a_0 for both individual crystals.

Then, the lattice parameters c_{ip} and a_{ip} corresponding to the points of inflection on $E_{tot}(\varepsilon)$ dependences for composites were used for calculations of axial stresses σ_f (σ_m) in fibers (matrix). The shapes of individual crystals of W and V must be, in an aggregate, accommodated to the predicted shape of the composite. This can be done by assuming bulk materials of tetragonal elementary cells with effective edge lengths c_{ip},

$$a_f = \lambda a_{ip} / 4$$

and

$$a_m = \sqrt{\frac{a_{ip} - a_f x}{1 - x}} .$$

Such elementary cells were found to be subjected to triaxial stresses with axial tensile components σ_f or σ_m and transverse (internal) components $\sigma_{tr.}$ The latter components are tensile for vanadium and compressive for tungsten. For vanadium, the stress σ_{tr} increases with increasing tungsten concentration in the composite. The stress (2) can be then evaluated as

$$\sigma = \sigma_f x\lambda^2 + \sigma_m (1 - x\lambda^2) .$$

Such obtained stress values were added to Fig. 3 (the crosses). It is evident that the values are systematically above the linear function interpolating strengths of W and V (the dotted line). However, they do not fully reproduce the computed σ_{ip} values of the composite. This means that either the λ ratio needs to be determined in a different way or the predicted synergy effect is not only caused by the influence of internal transversal stresses induced during the axial tensile deformation owing to different Poisson contractions of individual composite constituents. Therefore, other possible reasons should be studied in the future.

Conclusion

Elasticity and strength of nano-fiber reinforced composites under uniaxial loading parallel to the fibers were studied by means of first principle calculations. Computed results show that the bulk and the Young's moduli almost linearly

increase with increasing tungsten concentration. These results reveal that, in case of an ideal composite, the validity of linear mixture rule (1) for η = 1 is theoretically justified. Similar increasing dependence can be found in case of theoretical strength. In this case, however, the value corresponding to the strength of pure tungsten is reached already at about 60% atomic concentration of tungsten and then the computed values seem to become saturated. The influence of transverse biaxial stress coupling effect at the fiber/matrix interface gives only a partial explanation of the synergy effect.

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