

Ideal strength of a Cu multi-shell nano-wire

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Abstract

The ideal strength of a nano-component, which is the maximum stress of the structure, provides an insight into minute material. We conducted tensile simulations for a cylindrical-shaped Cu nano-wire composed of an atomic chain as a core wrapped around by shell(s) with the structure of (111) layers in a fcc crystal. Young's moduli and the ideal strengths of the wires are less than a single atomic chain and sheet. The mechanical strength of the wire is weakened by the following three factors: (a) changes in electron arrangement caused by combining core and shell; (b) a larger interatomic distance (inherent tensile strain) of the outer shell introduced for combining with the core chain; and (c) weak bonding (gap) on the outer shell caused by the mismatch of atomic layers due to the curvature difference. Factor (a) weakens the bonding of the shell(s) that occupy a greater part of the wire. A 5-1 wire, which consists of a core and a shell, is weakened compared with the single atomic chain and the single sheet due to (a) and (b). A 10-5-1 wire, consisting of a core and two shells, has less strength than a 5-1 wire due to (c) in addition to (a) and (b).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ideal strength is originally defined as the stress or the strain at which a perfect crystal becomes mechanically unstable under homogeneous deformation [1]. In analysis, a minimum unit cell is used to accomplish perfect homogeneous deformation. Ideal strength, which is the maximum stress that a bulk material can hold, gives a reference for the mechanical property [2].

Recent developments in the fabrication technology of nano-devices have enabled us to obtain nano-components with atomistic-scale structures. These materials have such shapes as films, tubes or wires in atomistic scale, and they sometimes have an exotic atom arrangement (microscopic structure) that differs from the bulk. Note that the dimensions of the overall shape of the nano-structure as well as the microscopic structure is in nanometres in these components. Because the strength of the component greatly depends on its shape in general, not only the

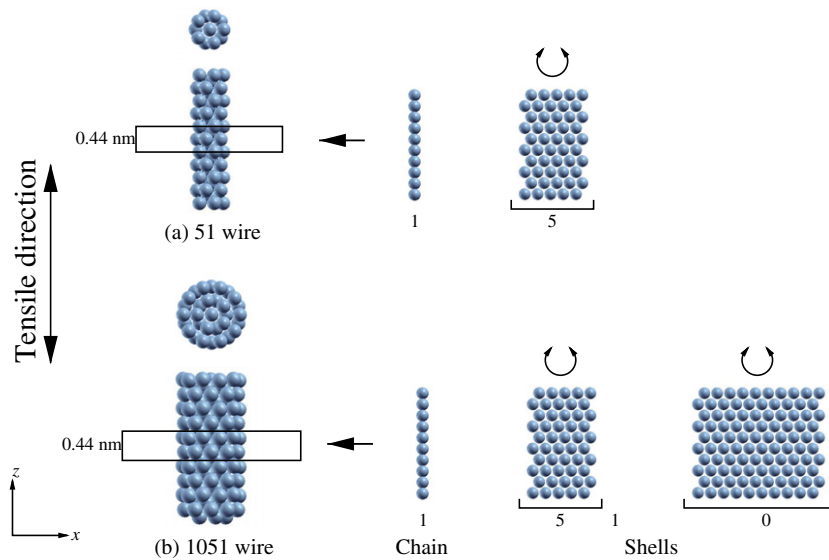


Figure 1. Multi-shell Cu nano-wires simulated. (a) a 5-1 wire composed of an atomic chain and a single sheet. (b) a 10-5-1 wire composed of an atomic chain and double shells.

microscopic structure but also its shape must be taken into account to evaluate the mechanical property.

Although nano-components do not have three-dimensional periodicity as a single crystal, they have highly symmetric structures. Nano-components without defects except for the surface can be considered to be of ‘ideal structure [3].’ The strength of ideal-structured material under homogeneous deformation can give a reference for the mechanical property as maximum attainable stress [4].

The structures of Cu nano-wires have been studied both by theoretical analyses and experiments [5–9]. Hwang and Kang [6] have suggested the stability of Cu multi-shell nano-wires, as shown in figure 1. González *et al* [8] observed the formation of an exotic pentagonal structure at the necking part during the tension of a thin Cu fcc single crystal, which suggests multi-shell structure. These results indicate the possibility of Cu nanowires with unusual microscopic structures that differs from the fcc structure. In this study, we evaluated the ideal strength of a Cu nano-wire with high-symmetric structure under tension.

2. Simulation models and procedure

The wires simulated have a single atomic chain at the centre around which a sheet (5-1 wire) or two sheets (10-5-1 wire) with a structure of (111) layer in a fcc crystal of Cu are wrapped. Here, periodicity along the z axis is identical for the core and the shell. Although the wire might have different periodicity for the core and the shell, in this paper we focus on the ideal structure of the wire and examine its possible structure since a Cu nano-wire with a more complex structure is beyond our focus. Therefore, the models shown in figure 1 were selected. Tensile simulations are conducted not only for the Cu nano-wires but also for their components, the atomic chain and the sheet. To evaluate the effect of curvature on the strength of the wire, a simulation for the shell of a 5-1 wire was conducted. The solid boxes shown in figures 1 and 2 indicate calculation cells. The unit cells of the 5-1 wire, the 10-5-1 wire, the chain, the

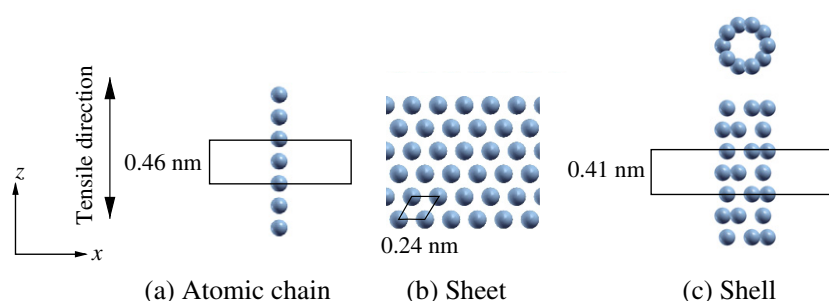


Figure 2. Simulation models of a Cu atomic chain, sheet and shell.

sheet, and the shell contain 12, 32, 2, 1 and 10 atoms, respectively, and the periodic boundary condition is applied to the x , y , and z directions. The sizes of the vacuum regions are large enough so that interaction between the neighbouring wires (sheets) is negligible.

After calculating the equilibrium structure at the unloaded state, a small tensile strain is applied to the model by elongating the simulation cell in the z direction and the atomic structure is relaxed by a conjugate gradient method. Repeating incremental straining $\Delta\epsilon_z$ and relaxation, tensile behaviour is simulated.

All the simulations in this study were conducted by the first principles (*ab initio*) code, VASP [10, 11], which uses plane wave basis sets with ultrasoft pseudopotentials [12]. The cut-off energy was 350 eV, and GGA (generalized gradient approximation) parametrized by Perdew and Wang [13] was used to estimate the exchange-correlation energy. For the wires and the chain models, $2 \times 2 \times 9$ k -point sampling grids were selected based on the Monkhorst–Pack method [14] and $21 \times 21 \times 2$ for the sheet. To verify the reliability of the calculation, equilibrium lattice constant a_0 and the elastic coefficients C_{11} and C_{12} under unloaded condition were preliminarily evaluated for a Cu single crystal. The results, 0.364 nm of a_0 , 170 GPa of C_{11} , and 127 GPa of C_{12} are in good agreement with the experimental data, 0.361 nm, 168 GPa, and 121 GPa [15, 16], respectively.

3. Results and discussion

The distance between the core chain and the surface shell in the 5-1 wire under no external load is 0.22 nm. In a 10-5-1 wire those between the core and the middle shell, and the middle and the surface ones, are 0.22 nm and 0.20 nm, respectively. These are close to the interlayer distance between (111) layers in a Cu single crystal of 0.21 nm. The atom pitch of the core chain in the 5-1 and the 10-5-1 wires is 0.22 nm, which is 4.3% shorter than the single atomic chain without the shell, 0.23 nm. On the contrary, the distance between the nearest neighbour atoms in the shells of the wires is 0.26 nm, which is 8.3% longer than the Cu sheet, 0.24 nm. Thus, the core chain and the shells of the wires have shorter and longer interatomic distances (compressive and tensile strain), respectively, at the equilibrium state in comparison with the single chain and sheet.

Figure 3 shows the stress–strain relationships of Cu wires, the chain and the sheet in tension. To evaluate the stress, we roughly estimate the cross-section areas of the wires, assuming that the outer shell possesses the area shown in the schematic illustration, figure 4. Here, a_0 is the distance between (111) planes in a Cu single crystal, 0.21 nm. Though ambiguity remains in the cross-section assumption for the precise investigation, the evaluation method

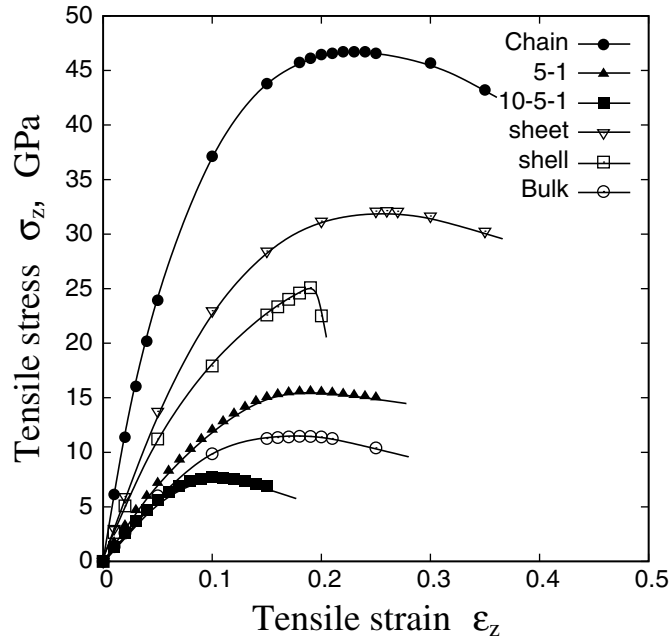


Figure 3. Stress–strain relationships of Cu wires, a chain, and a sheet in tension. Bulk and shell results are shown for comparison.

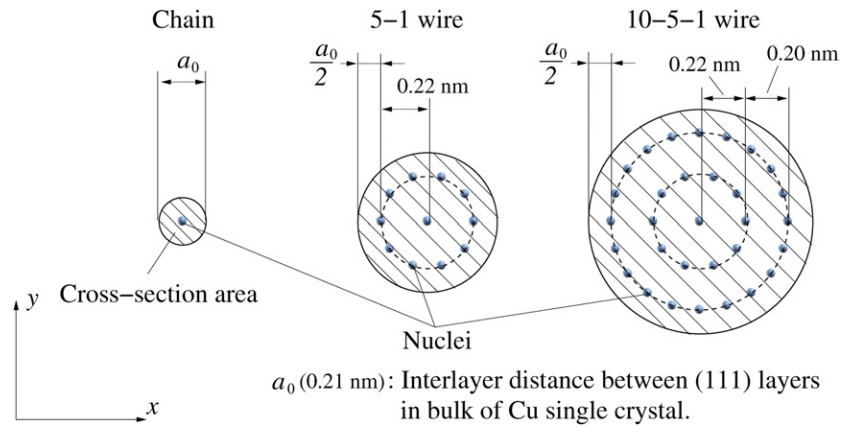


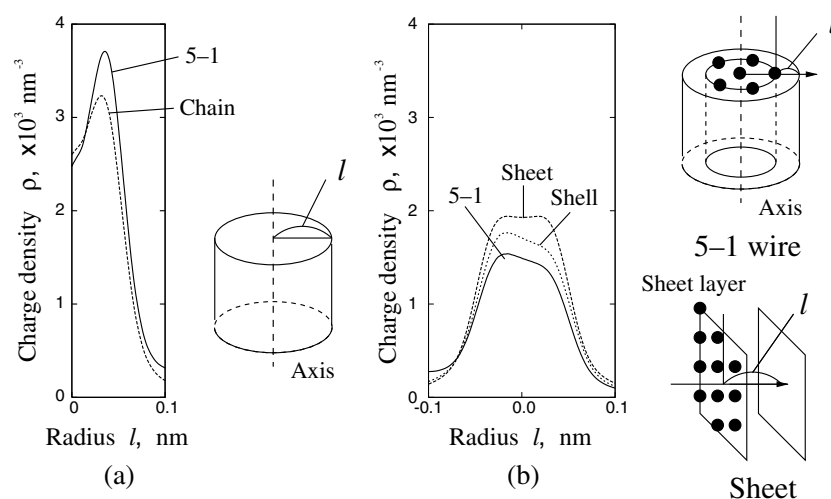
Figure 4. Schematic illustrations of cross-section areas of simulation models.

could not make large differences in the calculated stress and affects only slightly the following discussions.

Young's moduli at the equilibrium state, the ideal strengths and the critical strains (strains at maximum stress) evaluated from the stress–strain relation (figure 3), are listed in table 1. The Cu bulk results under tension of $[11\bar{2}]$, which corresponds to those for the sheet and the wires, are shown for comparison. Young's moduli of 5-1 and 10-5-1 wires are smaller than the chain and the sheet. In a macroscopic composite material that consists of elements with different elastic moduli, the modulus of the composed structure is approximately given by the

Table 1. Young's moduli, ideal strengths, and critical strains of Cu chain, 5-1 wire, 10-5-1 wire and the sheet. The results of bulk and shell are also shown for comparison.

	Chain	5-1	10-5-1	Sheet	Shell	Bulk
Young's modulus (GPa)	628	178	140	310	275	137
Ideal strength (GPa)	46.7	15.6	7.71	32.2	25.1	11.5
Fracture strain	0.23	0.19	0.10	0.26	0.19	0.18

**Figure 5.** Average charge densities at radius l from the axes of a 5-1 wire. (a) Density near core compared with results of single atomic chain. (b) Density near shell compared with results of the sheet and the shell.

mixture rule. Although the rule indicates Young's moduli of 344 GPa and 322 GPa for 5-1 and 10-5-1 wires, respectively, it is clear that they are far off the mark. The mechanical property of the wire cannot be explained by simply combining the chain and sheet results. This suggests that electron distribution, which is sensitive to atom arrangement, plays an important role in the mechanical property. Note that the difference in Young's moduli of the shell and the sheet is small, which indicates that the reduction in the strength of the 5-1 wire cannot be explained by curvature of the shell.

Figure 5 shows the circumferential average of electronic charge density at radius l of the 5-1 wire compared with the chain (figure 5(a)) and the sheet, and the shell (figure 5(b)). In the wire, charge density near the core is higher than the chain, and the shell has lower density than the sheet, because the core and the shell have shorter and longer interatomic distances, respectively, than the chain and the sheet. The outer region of the shell has a lower charge density than the inside because the curvature of the shell causes the outer part to have extended volume and to compress the inner part. However, the curvature effect on the weakening of the wire can be considered slight. To observe the effect of combining the core and shell on the electronic structure, the difference between the charge density distribution of the 5-1 wire and the core and the shell alone is calculated. The results are shown in figure 6. Charge density decreases at the core and the shell of the 5-1 wire and increases at the region between them, which indicates that electrons shift between the core and the shell to combine them. Thus the simple mixture rule does not work, and these changes in the electron arrangement contribute to the decrease in Young's modulus.

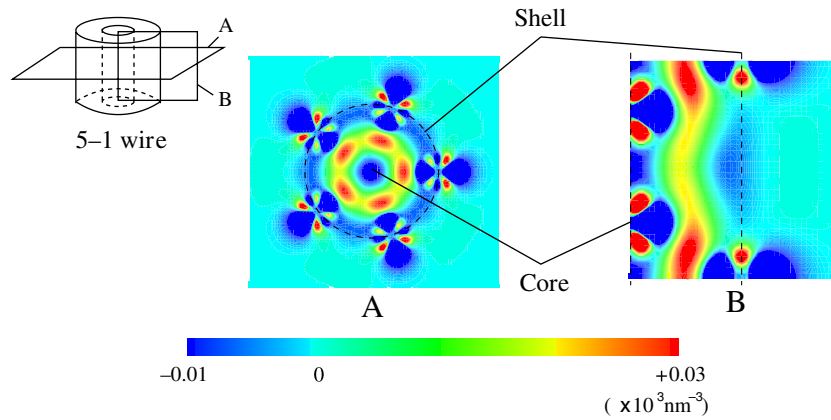


Figure 6. Difference in charge density distribution between a 5-1 wire and free-standing core and shell.

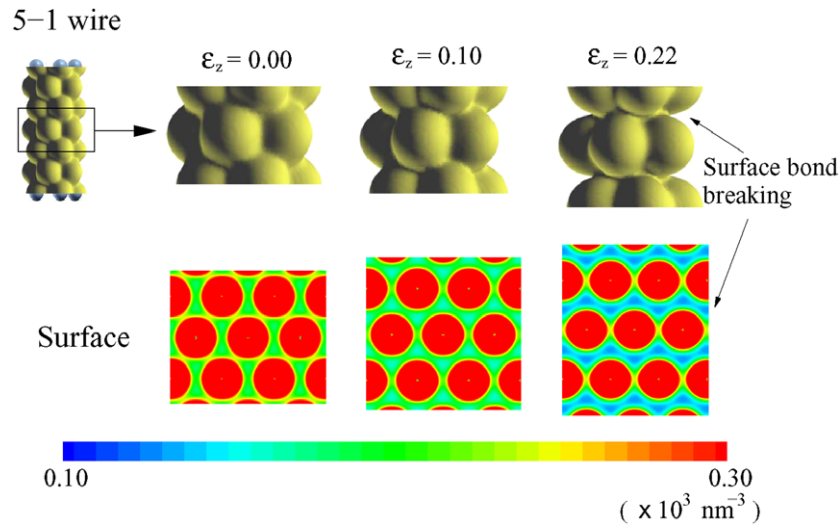


Figure 7. Change in atomic structures and charge density distributions during tension of a 5-1 wire. The isosurface of $0.16 \times 10^3 \text{ nm}^{-3}$ is extracted in the upper graphs while distributions on the shell are shown in the lower ones.

As shown in figure 3, the ideal strength of the wires is lower than the chain and the sheet. The change of the electron arrangement (figures 5 and 6) again contributes to strength reduction. Figure 7 denotes the change in the electronic structure (isosurface of $0.16 \times 10^3 \text{ nm}^{-3}$) during tension [17]. It shows the fracture initiates from the shell. When electronic bonds at the shell are broken, the core still sustains the load. Since the simulation was conducted under strain (displacement)-control, a catastrophic fracture did not take place. Under load-controlled simulation, however, an instant fracture may occur at peak stress.

Figure 3 indicates that the wires become unstable at lower strain than the chain and the sheet. Lower critical strain can be approximately explained by the longer interatomic distance of the shell at the equilibrium state. At the critical point of the 5-1 wire, the interatomic distance of the shell is almost equal to the sheet at its fracture strain. Although the core in the

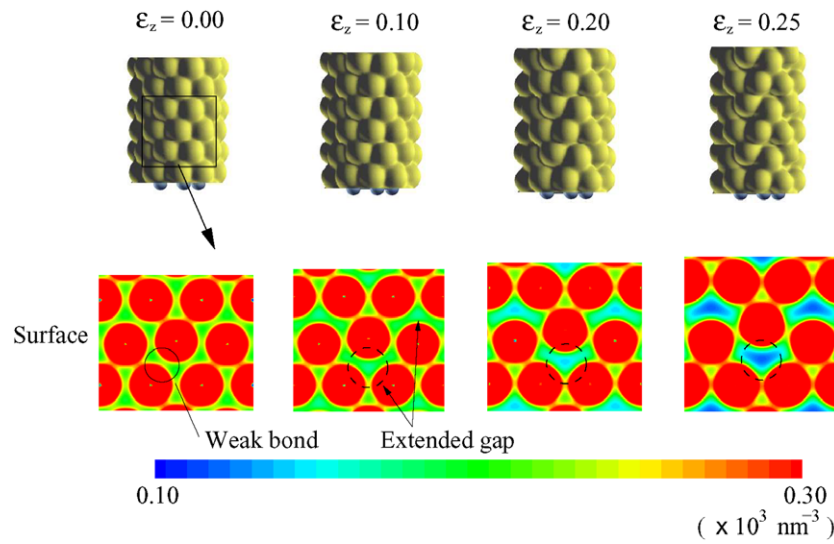


Figure 8. Change in atomic structures and charge density distributions during tension of a 10-5-1 wire. The isosurface of $0.16 \times 10^3 \text{ nm}^{-3}$ is extracted in the upper graphs while distributions on the shell are shown in the lower ones.

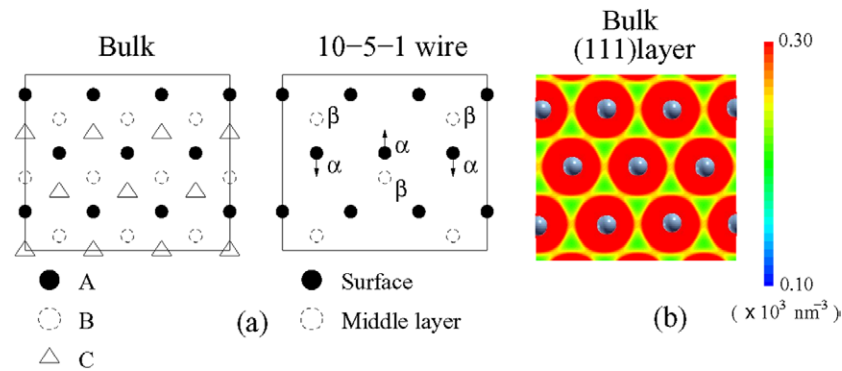


Figure 9. Schematic illustration explaining deviation of surface atoms of a 10-5-1 wire (a) and charge density distribution of (111) layer of bulk at $\varepsilon_z = 0.00$ (b).

wire has compressive strain at the initial point, the sheet layer contains most of the atoms in the wire. In the wire, early breaking of bonds at the surface layer due to the longer interatomic distance of the shell at equilibrium and the change in electron arrangement lowers the wire's ideal strength compared with the chain and the sheet.

A 10-5-1 wire has lower ideal strength and lower critical strain than a 5-1 wire. Figure 8 shows the isosurface of $0.16 \times 10^3 \text{ nm}^{-3}$ and the charge density on the shell. The bonds are non-equivalent even at $\varepsilon_z = 0.00$, and the lower charge density between atoms indicated by the dotted circle suggests a weak one. As the strain increases, the gap grows at the marked region and causes a break in the outer shell. This is different from the fracture process on the shell of the 5-1 wire, where deformation is homogeneous during tension (figure 7). This further reduces the strength in the 10-5-1 wire.

Although the 10-5-1 wire has two shells ((111) layers), its structure is different from the stacking of (111) layers in a single crystal. Figure 9 shows atom configurations on each

layer. While the bulk possesses the stacking of (111)s as A, B, C, A, . . . , the atoms in the surface shell of the wire are not stacked on the perfect lattice points because the number of atoms along the circumference is different between the surface shell and the inner shell due to their curvature. This causes atoms α to deviate from the symmetric point toward the arrows indicated in the figure. Although this shift of atom α is minute (0.008 nm in the z direction), it creates unbalanced bonding at $\varepsilon_z = 0.00$, as indicated in figure 8. The subtle mismatch weakens the strength of the surface layer and causes early initiation of fracture. Of course, changes in electron arrangement and larger interatomic distance are also responsible for the lower strength in the 10-5-1 wire.

4. Conclusion

First principles simulations of Cu nano-wires, which consisted of the core atomic chain and the shell(s), were conducted under tension, and their ideal strengths were evaluated. The fracture process is investigated to understand the differences in strength. The results are summarized as follows.

- (1) At the equilibrium state, the distance between the core and the shell and between shells in the wire is almost equal to the inter-(111) layer distance of the bulk. However, the core and the shell have shorter and longer interatomic distances (inherent compression and tension), respectively, than the chain and the sheet, at the unloaded state.
- (2) Young's modulus of the wire is smaller than the single chain and the single sheet. Young's modulus of the wire cannot be calculated by the mixture rule using the chain and the sheet because the electrons in the shell(s) have shifted toward the core chain, and the electronic bondings on the shell, which occupy a greater part of the cross-section, are weakened.
- (3) Ideal strength and the critical strain of the wire are lower than those of the single chain and the sheet. The 10-5-1 wire is weaker than the 5-1 wire. There are three factors lowering the strength of the wires: (a) change in electron arrangement caused by combining core and shell (see item (2)); (b) larger interatomic distance (inherent tensile strain) of the shell (see item (1)); and (c) weak bonding (gap) on the outer shell caused by the mismatch between shells due to curvature difference.
- (4) In the 5-1 wire, the decrease in strength is attributed to (a) and (b).
- (5) In the 10-5-1 wire, the gap (c) on the outer shell extends under tension and this initiates the local fracture. This inhomogeneous breaking of bond (factor (c)) in addition to (a) and (b) results in the decrease of strength.

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