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Ultralow Thermal Conductivity and Thermal Stress of Ceramics with Surface Nanowire-structures

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An analytical model on the size and fraction dependent thermal conductivity, elastic modulus and thermal stress of nanowire-composites are developed, and the theoretical prediction agrees with the experimental results of Si nanowires. And the model proposes that the high thermal shock strength of ceramics can be achieved by surface nanostructurization, which is related to the low thermal conductivity and thermal stress of the nanostructures and voids. The theory will be helpful to guide design of thermal barrier coatings.

Keywords: Nanowires, Thermal conductivity, Elastic modulus, Thermal stress.

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1. INTRODUCTION

The low thermal conductivity is one of important properties for thermal barrier engineering and thermoelectric devices, etc. The experimental study has indicated that the thermal conductivity of semiconductor single-crystal nanowires and thin films [1-4], multilayers [5], and ceramic coats with nanostructures [6] is much lower than that of the corresponding bulk materials. The theoretical mechanism behind the low thermal conductivity was discussed based on the phonon confinement and the surface/interface scattering effects related with the reduced size and the increased surface/interface ratio of the nanoscale structures [2,7-9]. Recently, the high strength of the ZrB_2 ceramics resisting the high temperature thermal shock was achieved by the surface disposal, and the surface structure consists of the nanowires and the voids [10]. What's the underlying physical mechanism of the high thermal shock strength? What's the relation between the phenomenon and the low thermal conductivity nature of the surface nanostructure? In this paper, the analytical models on the wire diameter and pore fraction dependent thermal conductivity, and on the fraction dependent elastic modulus and thermal stress of nanowire-composites are developed, and the theoretical prediction agrees with the latest experimental results well. And the model explains that the high thermal shock strength is related to the low thermal conductivity and thermal stress of the surface nanostructure.

2. THE MODEL ON THE SIZE-DEPENDENT THERMAL CONDUCTIVITY

According to the kinetic formula of the thermal conductivity $k = 1/3Cvl$, where C is the specific heat, v is the average phonon velocity, and l is the phonon mean free path, considering the phonon confinement and the boundary scattering effect induced by the small size and the large surface ratio, the thermal conductivity k_n of thin films has been derived by introducing the intrinsic size effect of v and l and combining with the surface scattering effect [7]. k_n is expressed as

$$k_n k_b = p\exp(-l_0/D)\ \exp\left[(1-\beta)/(D/D_0-1)\right]^{3/2} \tag{1}$$

where k_b is the corresponding bulk value, $0 < p = 1\text{-}10\eta/D \le 1$ is the surface roughness coefficient reflecting the scattering degree, η is the surface rough thickness and D is the thickness of the thin films [7], l_0 is the phonon mean free path of the crystals in Debye model, $\beta = 2S/(3R) + 1 > 1$ is the atomic vibration parameter with the ideal gas constant R and the vibration entropy of melting $S = H/T_0\text{-}R$ [7], H is the melting enthalpy and T_0 is the melting temperature of the crystals, $D_0 = 6h$ is the minimum critical size of thin films with the atomic diameter h [7]. Equation (1) indicates that the thermal conductivity of thin films decreases with reducing thickness, and the formula has been validated by the molecular dynamic simulation and the experimental results [1-2,7].

Recently, the ultralow thermal conductivity and enhanced thermoelectric performance of Si nanowires was achieved in the latest experiments [3-4]. Let's explain the low thermal conductivity based on the Eq. (1). Differently, k_n in the equation denotes the thermal conductivity of nanowires, D represents the diameter of nanowires, and $D_0 = 4h$ is the minimum critical size of nanowires [7]. Figure 1 shows that the latest experiment measurement with the smaller diameters [4] and the previous one with the larger diameters [1] obtained by the same preparation method are both in agreement with the prediction of Eq. (1) with roughness parameter $p = 1 - 10\eta/L = 0.4$ (where the mean surface roughness height η is about 1.32 nm, and the diameter of the nanowire $L = 22$ nm [1]), and both experiments correspond

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to the smooth surface and the small roughness of the nanowires. The other latest experiment measurement realized the ultralow thermal conductivity by the surface larger roughness of the nanowires [3], which is in agreement with the prediction of the model at $p = 0.07$, which can also be seen from Fig. 1. In the experiment, the surface roughness is larger than that in Refs. [4] and [1] as mentioned in Ref. [3]. According to $p = 1\text{-}10\eta/L = 0.07$, η is about 4.65 nm ($L = 50$ nm [3]), which agrees with the experimental observation [3] (the mean roughness height 1 – 5 nm). According to the model, the larger

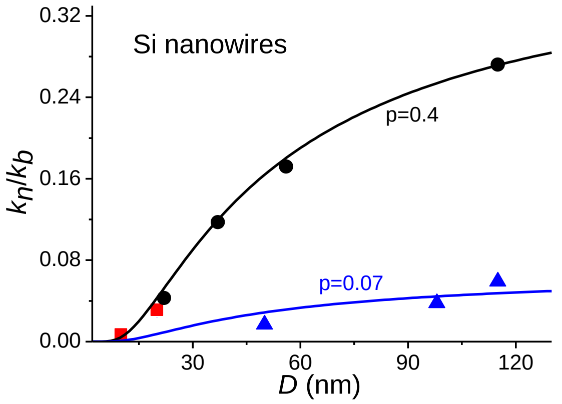

Fig. 1 – The diameter-dependent thermal conductivity of nanowires. The symbols are the experimental results at the room temperature: the triangles are the data cited from Ref. [3], the squares from Ref. [4], and the circles from [1]. The curves are the model's predictions. $H = 50.55$ KJmol^{-1}, $T_0 = 1685$ K, $l_0 = 41$ nm, and $h = 0.3368$ nm in Eq. (1) [7]

roughness corresponds to the smaller p, and the larger scattering, thus the smaller thermal conductivity. p decreases about 5 times (from 0.4 to 0.07) due to the larger roughness, which also agrees with the experiments that the thermal conductivity is about 5 times lower [3] (EE Si nanowires exhibit a diameter dependence of thermal conductivity k similar to that of VLS-grown wires. The magnitude of k, however, is five to eightfold lower for EE nanowires of comparable diameters [3]), since the thermal conductivity is proportional to p according to Eq (1).

3. THE EXPLANATION TO THE HIGH THERMAL SHOCK STRENGTH

In a recent report, the high strength of the ZrB_2 ceramics resisting the high temperature thermal shock was achieved by the surface disposal with the surface structure consisting of the nanowires and the voids [10]. The authors attributed it to the hydrophobic surface structures. The water may not able to contact directly the heat specimens with the surface nanowires during quenching in cool water, thus the strength is retained compared to the initial bulk samples [10]. However, if the specimens are not placed into water, how about is the strength of the ceramics? This question urges us to think further the underlying physical mechanism, let's discover how the nanowires and the voids play important role in the thermal protection things.

3.1 Ultralow Thermal Conductivity

According to the model, the thermal conductivity of the ZrB_2 nanowires reduces greatly due to the larger surface roughness (see Fig. 2b in Ref. [10]) and the smaller diameter D of 81.5 nm [10]. The surface rough thickness η is about 8 nm [10], thus $p = 1\text{-}10\eta/L = 0.02$, and the thermal conductivity of the nanowires k_n is smaller than 2% of κ_b in terms of Eq. (1) combining with the size effect of nanowires (the exponent term), i.e., $\kappa_n < 1.2$ Wm^{-1}K^{-1} since κ_b is 60 Wm^{-1}K^{-1} [10].

Furthermore, besides the nanowires, the deposed surface also contains a great deal of voids [10]. The effective thermal conductivity k_e of the composites including the nanowires and the voids is expressed as

$$k_e = f_n k_n + f_p k_p \qquad (2)$$

based on the parallel model considering that the nanowires stand up almost vertically on the surface of the ceramics [10], where $f_n = 0.37$ and $f_p = 0.63$ [10] denoting the fraction of the nanowires and the voids, respectively, k_n and k_p represent the thermal conductivity of the nanowires and the voids, respectively. $k_p = 0.0262$ Wm^{-1}K^{-1} for air [9], even $k_n = 1.2$ Wm^{-1}K^{-1}, $\kappa_e = 0.46$ in terms of Eq. (2), thus the thermal conductivity of the composits is smaller than 0.46 Wm^{-1}K^{-1}, which is lower than κ_b of 60 Wm^{-1}K^{-1} more than two orders. Moreover, the parallel model predicts the upper limit, if the suface sructure contains some unorderly nanowires with random orientation, the thermal conductivity will be lower [9]. Therefore, the surface with the nanostructures is similar to an excellent thermal barrier coating, which protects the specimens and makes them not suffer the sharp temperature change during quenching, thus the strength of the ceramics is retained.

3.2 Ultralow Thermal Stress

The high thermal stress σ_b was produced in the initial bulk specimens during quenching, and is expressed as $\sigma_b = \alpha_b(\Delta T)E_b$ based on the equivalent stress consideration corresponding to the thermal strain, where $\alpha_b = 6.7 \times 10^{-6}$ K^{-1} [11] is the thermal expansion coefficient of the ZrB_2 ceramics, ΔT denotes the temperature change, $\alpha_b\Delta T$ represents the produced thermal strain, E_b is the elastic modulus of the bulk ceramics and is about 245 GPa [11]. Since the strength of the specimens decreases when the heating temperature is above 673 K [10], $\Delta T = 673 - 293 = 380$ K during quenching at the ambient temperature of 293 K [10]. Therefore, the thermal stress σ_b is 623.8 MPa, close to the intrinsic strength of the ceramics 738.6 MPa [10], such high residual thermal stress reduces the strength of the specimens, and the result agrees with the measured data that the residual strength is only 105.4 MPa [10]. Even $\Delta T = 200$ K (the lower limit [10]), the produced minimum thermal stress (328 MPa) is also larger.

Differently, the low thermal stress σ_n was produced in the specimens after the surface disposal, $\sigma_n = \alpha_n(\Delta T)E_n$, which is mainly resulted from the decreased elastic modulus and the thermal expansion coefficient of the composites including the nanowires and the voids. Based on the self-consistent effective medium theory [12], the effective modulus E_n of the nanowire-composites is expressed as

$$\sum_{i=1,2} f_i \frac{E_i - E_n}{3E_i + 4G_n} = 0 , \tag{3.1}$$

$$\sum_{i=1,2} f_i \frac{G_i - G_n}{5G_n(3E_i + 4G_n) + 6(E_n + 2G_n)(G_i - G_n)} = 0 , \tag{3.2}$$

where $E_1 = E_b = 245$ GPa and $E_2 = 0$ (for air) denote the bulk modulus of the nanowires and the voids, respectively, $G_1 = 240$ GPa [11] and $G_2 = 0$ denote the shear modulus of the nanowires and the voids, respectively, $f_1 = 0.37$ and $f_2 = 0.63$ [10], G_n is the shear modulus of the composites. According to Eq. (3), $E_n = 11$ GPa and $G_n = 16$ GPa. The result indicates the elastic modulus of the composites decreases more than one order compared with E_b due to a great deal of voids, which can also be seen from Fig. 2.

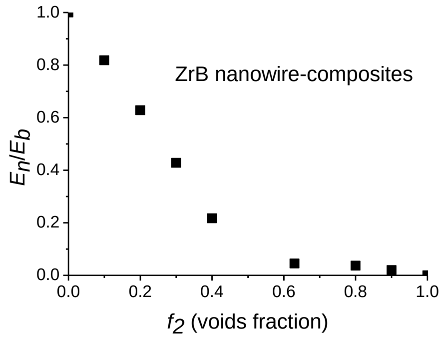

Fig. 2 – The fraction-dependent elastic modulus of the composites including nanowires and voids. The symbols are the calculation results based on Eq. (3)

On the other hand, the thermal expansion coefficient α_n of the composites decreases since the nanowires can expand freely and the voids can accommodate the strain. Even $\alpha_n = \alpha_b$, when $\Delta T = 380$ K as the same as above, $\sigma_n = 28$ MPa, which is lower than σ_b of 623.8 MPa more than one order. This thermal residual stress is much lower than the intrinsic strength of the ceramics, thus the strength can be retained. Even $\Delta T = 3000$ K (the upper limit [10]), the produced maximum thermal stress (221 MPa) is also lower than the minimum thermal stress produced in the initial bulk specimens. Therefore, the ceramics with the surface nanostructures is favorable to retain the high strength resisting high temperature thermal shock. In fact, the enhanced thermal shock resistance of the nanostructured ZrO_2 has also been achieved [13], which is just resulted from that the nanostructure reduces the thermal conductivity and thermal stress (discussed in our other manuscript), thus protects the samples during the thermal shock.

4. CONCLUSION

In summary, the simple models on the size and fraction dependent thermal conductivity of nanowires and its composites, and on the fraction dependent elastic modulus and thermal stress of the nanowire-composites are developed. The prediction based on the model agrees with the experimental measurement of Si nanowires, the thermal conductivity decreases with reducing diameter and increasing surface roughness. The theoretical model explains the mechanism of high thermal shock strength of ZrB_2 ceramics with surface nanowire-structures, which is related to the low thermal conductivity and thermal stress of nanostructures and the voids. The analytic models can bridge the nanoscale physics and nanoscale engineering application simply.

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