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A new model for the effect of grain size on the elastic modulus of nanocrystalline materials

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A new model is developed for the structure of nanocrystalline materials. Based on the developed model, a new approach for investigating the effect of grain size on the elastic moduli of nanocrystalline materials is introduced. The predictions of the model are strongly correlated with the experimental results reported in the existing literature.

Key words: *nanocrystalline materials; grain size; elastic modulus*

1. Introduction

The effect of grain size on the non-elastic properties of nanocrystalline materials (NCMs) is quite well understood; however, the effect of grain size on the elastic properties of NCMs is still not known [1, 2]. Some experimental results indicate a decrease in Young's modulus with a decreasing grain size, although some other results show almost no grain size effect [3]. In order to investigate the effects of grain size on the elastic modulus of NCMs, some investigators treated NCMs as composite materials with a grain interior phase and inter-grain phase (sometimes including grain boundaries, triple lines, and quadruple nodes) [3, 4]. Moreover, molecular dynamics simulations (MDS) have also been successfully used to investigate the effect of grain size on the elastic properties of NCMs [1]. Nevertheless, it seems that to investigate the effect of grain size on the elastic properties on NCMs, an accurate concept of the structure of NCMs is needed. Thus, the main aim of this work is an attempt to introduce a new approach to model the structure of NCMs. It is assumed that a nanocrystalline structure could be considered as a layered composite. This can be considered as a novel approach to model the structure of nanocrystalline materials. Moreover, by using this model, a new relation between the grain size and elastic modulus of NCMs is introduced.

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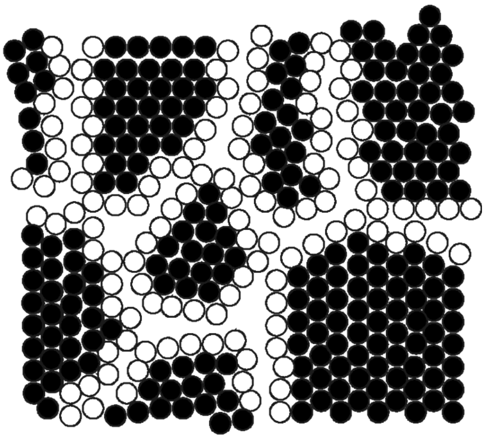
2. Model

The concept of NCMs was put forth by Gleiter [5, 6]. In Figure 1 (left) the concept of an NCM structure is schematically shown. Generally, the structure of NCMs can be divided into two parts: grain core and grain-boundary layers. Figure 1 (right) shows how the relative proportions of these two regions vary with the grain size. The important point is that as the grain size decreases into the nanocrystalline region, the grain-boundary layers dominate the structure of NCMs [7].



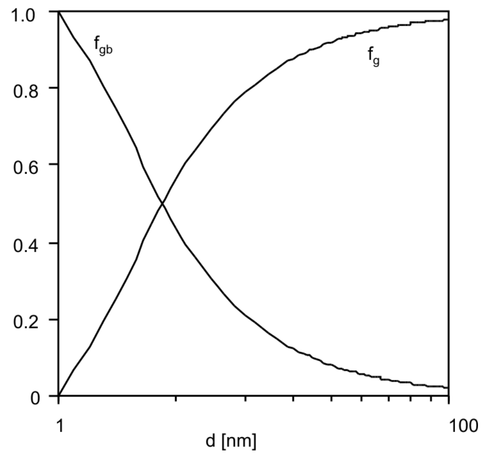


Fig. 1. A simple two-dimensional model of nanocrystalline materials (left).
The atoms in the bulk of the grains are indicated in black. The atoms in the grain boundaries are represented as open circles [5]. The volume fraction of grain-boundary layer (f_{gb}) and the volume fraction of crystalline grain (f_g) versus the grain size (d)

According to the conceptual model of NCM structure, as given above, it can be assumed that grain boundaries are like thin layers which bind and fix the nanometer grains. This assumption is more convincing when we consider a considerably high volume fraction of grain boundaries as the grain size decreases into the nanocrystalline region. Our model is based on this assumption. The structure of NCMs can be considered as follows (Fig. 2):

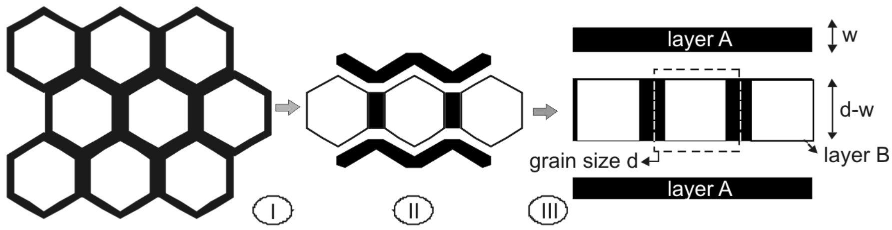


Fig. 2. Models of NCM : I – a simple two-dimensional model,
II – model considering grain boundary layers as thin layers which bind and fix the nanometer grains, III – a simple model of the structure of NCMs

We consider NCMs as laminated composites with the following layers (Fig. 2 (III)): Layer A which is a grain-boundary layer with width equal to w (grain-boundary width); layer B which is treated as a fibre-composite layer where the matrix consists of grain-boundary layers, and fibres are grain cores; the width of layer B is equal to d-w ($d - 2w/2$). The model presented in Fig. 2 (III) enables one to predict elastic moduli of NCMs.

3. Elastic modulus

According to Fig. 2 (III) and by applying the laws of classical mechanics to the laminated composite, Young's modulus of NCMs can be evaluated under the assumption that the nanocrystalline bulk is subject to a tensile stress acting in a direction perpendicular to layer A:

$$\frac{1}{E} = \frac{f_A}{E_A} + \frac{f_B}{E_B} \tag{1}$$

where E, E_A and E_B are Young's modulus of the bulk, layer A and layer B, respectively, and f_A and f_B are the volume fractions of layers A and layer B, respectively; Figure 2 (III) shows that f_A and f_B can be expressed as follows:

$$f_A = \frac{w}{w + (d - w)} = \frac{w}{d}, \qquad f_B = 1 - f_A = \frac{d - w}{w + (d - w)} = \frac{d - w}{d} \tag{2}$$

Figure 2 (III) shows that E_A is equal to E_{gb} (Young's modulus of grain-boundary layers) where E_B can be calculated from Eq. (3), assuming that the nanocrystalline bulk and layer B are subject to tensile forces acting in a direction perpendicular to layer B (Fig. 2)

$$E_B = f_M E_M + f_F E_F \tag{3}$$

f_M denotes the volume fraction of matrix (grain-boundary layers) in layer A and f_F denotes the volume fraction of fibres (grain cores) in layer A; E_M is Young's modulus of the matrix in layer A which is equal to E_{gb}; E_F in Eq. (3) shows Young's modulus of fibres in layer A which is equal to E_g (Young's modulus of grain cores). According to Fig. 3, the values of f_M and $f_{g\text{-}B}$ can be calculated by the following relations:

$$\begin{gathered} f_M = \frac{2\frac{w}{2}(d - w)}{(d - w)^2 + 2\times\frac{w}{2}\times(d - w)} f_B = \frac{w}{d}\times\frac{d - w}{d} = \frac{w(d - w)}{d^2} \\ f_F = (1 - f_{gb-B}) f_B = \frac{(d - w)^2}{(d - w)^2 + 2\times\frac{w}{2}\times(d - w)} \frac{d - w}{d} = \frac{(d - w)^2}{d^2} \end{gathered} \tag{4}$$

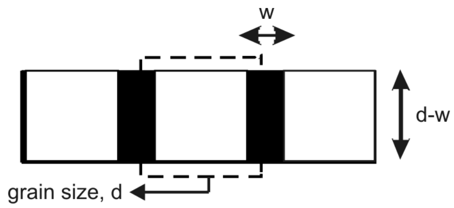


Fig. 3. Scheme of the layer B as used for calculating $f_{gb\text{-}B}$ and $f_{g\text{-}B}$

Therefore the values of Young's moduli of nanocrystalline materials can be calculated by substituting Eqs. (2)–(4) into Eq. (1):

$$\frac{1}{E}=\frac{\frac{w}{d}}{E_{gb}}+\frac{\frac{d-w}{d}}{E_{gb}\frac{w(d-w)}{d^2}+E_g\frac{(d-w)^2}{d^2}} \tag{5}$$

or

$$\frac{1}{E}=\frac{\frac{w}{d}}{E_{gb}}+\frac{d}{E_{gb}w+E_g(d-w)} \tag{6}$$

The important point about Eq. (6) is that it models the change of E with grain size. Equation (7) represents Eq. (6) where E is normalized to E_0 (or E_g) for the perfect crystal lattice

$$\frac{E_0}{E}=\frac{\frac{w}{d}}{\frac{E_{gb}}{E_0}}+\frac{d}{\frac{E_{gb}}{E_0}w+(d-w)} \tag{7}$$

It is generally accepted that the elastic modulus of the amorphous alloy is 60–75% or 70–80% of that of the corresponding equilibrium crystalline alloys [8, 9]. So the ratio E_{gb}/E_g is about 0.7. A similar ratio for E_{gb}/E_g is also assumed in previous works [1–4]. The change of E with grain size has also been modelled by Shen et al. [10] assuming that the modulus is influenced by the grain interior, grain boundary, and grain boundary triple junctions. Different contributions to Young's modulus are estimated according to the rule of mixtures for composite materials by considering their volume fractions. Equations (8) and (9) represent the upper and lower bounds of the rule of mixtures, where E is normalized to the E_0 for a perfect crystal lattice.

$$\frac{E}{E_0}=(1-V_{gb}-V_{tj})+Vgb\frac{E_{gb}}{E_0}+V_{tj}\frac{E_{tj}}{E_0} \tag{8}$$

$$\frac{E_0}{E} = (1 - V_{gb} - V_{tj}) + \frac{V_{gb}}{\frac{E_{gb}}{E_0}} + \frac{V_{tj}}{\frac{E_{tj}}{E_0}} \tag{9}$$

V_{gb} and V_{tj} are the volume fractions of the grain boundaries and triple junctions respectively; moreover, Shen et al. assumed E_{gb}/E_0 to be 0.7 and E_{tj}/E_0 to be 0.75. Figure 4 depicts the comparison between Eq. (7), Eqs. (8) and (9) and the experimental data. Figure 4 shows the calculated values of E/E_0 according to $E_{gb}/E_g = 0.7$ and $w = 1$ nm.

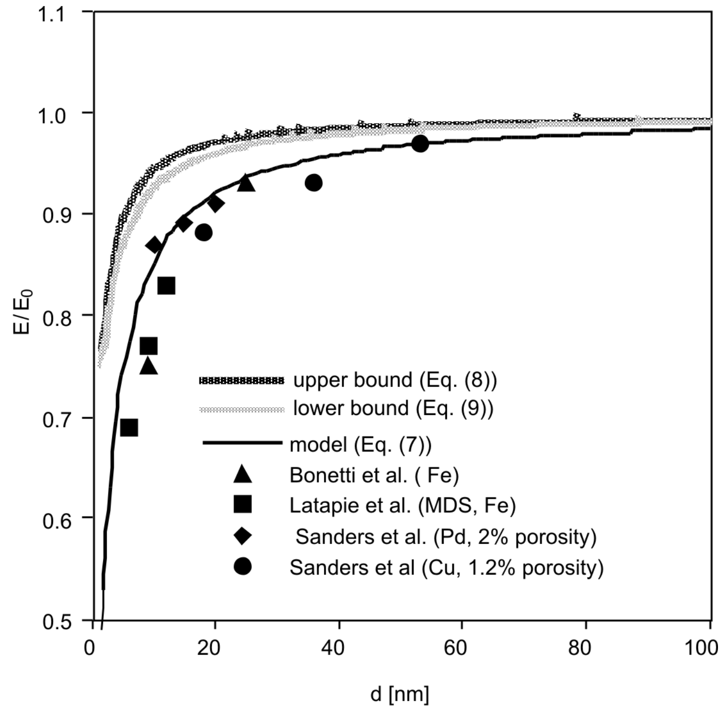


Fig. 4. Dependence of the E/E_0 ratio on the grain size for calculated values and previous works

From Figure 4 it can be concluded that elastic moduli of NCMs are essentially the same as those for conventional grain size materials until the grain size becomes very small (< 20 nm). Because grain boundaries occupy a larger fraction of the total volume in samples with smaller grain sizes, the decrease in E/E_0 could be attributed to the large number of atoms associated with grain boundaries and triple junctions. Since the elastic modulus is a measure of the bonding between the atoms, the reduction of E for both grain boundaries and NCMs can be explained in terms of the increased spacing between atoms in the grain boundaries and triple junctions [1, 13, 14]. The increased spacing between atoms in grain boundaries is schematically shown in Fig. 1 (left).

From Fig. 4 it can be seen that there is a good agreement between the experimental data and the predictions of the model; however, the values predicted from the model are lower than both those from the upper bond model and from the lower bond model. Figure 4 also shows that both the upper bond model and the lower bond model predict higher values than the experimental results. Latapie and Farkas assumed Young's modulus for the grain boundary and triple junction components to be 45% and 50%,respectively, of those of the grain interior, i.e., 45% for E_{gb}/E_0 and 50% for E_{tj}/E_0 [1]. Using these values, the calculated data are situated between the upper and lower bound of the rule of mixtures for composite materials [1]. When the grain size is 1 nm, E/E_0 is 0.75 (Fig. 4), being equal to the assumed value for E_{tj}/E_0. However, according to the presented model, E/E_0 is equal to 0.35 when the grain size 1 nm.

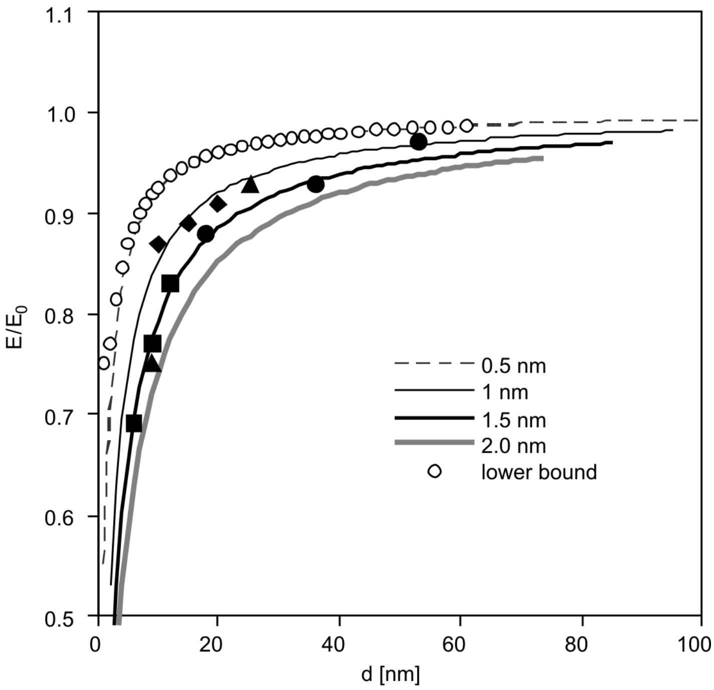


Fig. 5. The effect of grain boundary width on the ratio E/E_0

As an illustration of the effect of grain boundary width on E, Fig. 5 shows the results of calculation using Eq. (7), with w in the range of 0.5–2 nm. It can be seen from this figure that the higher the value of the grain boundary width, the lower the modulus of elasticity. That is because higher grain boundary thicknesses increase the value of f_{gb}. Therefore, the contribution of grain boundaries in the microstructure will be greater, and, because of the lower amount of E_{gb}, E will decrease.

Theoretically, there is a limit to the presented model; according to Fig. 3, the model is valid only for grain sizes (d) higher than grain boundary width (w). Another limit to the developed model is the lowest limit of the crystallite size (d) which leads to the instability of the crystallite structure with respect to the amorphous structure. Such a crystalline-to-amorphous transition has been found in silicon for a crystallite size of about 30 Å [15]. The thermodynamic criterion of such a transition has been discussed elsewhere [15].

4. Conclusion

A new composite model for the structure of nanocrystalline materials was presented. It was supposed that nanocrystalline materials could be considered as layered composites. Based on the model, a new approach to investigate the effect of grain size on elastic moduli of nanocrystalline materials was introduced. Results show that when the grain size is smaller than 20 nm, Young's modulus of a nanocrystalline material strongly decreases. The predictions of the model were compared with the experimental data, and a strong correlation was observed.

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