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Lattice distortion and its effects on physical properties of nanostructured materials

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Abstract

A theoretical model is developed to understand the basic mechanism of the deviation of a crystal lattice from the perfect structure in nanostructured materials. The interface tension and the stress field induced by the excess volume in the grain boundaries are the two main reasons for lattice distortion. Based on this model, the contribution of the lattice distortion to the thermal expansion coefficient of nanostructured materials is analysed quantitatively. The results show that the unusual physical properties of nanostructured materials result not only from grain boundaries, but also from nanocrystallites.

1. Introduction

Nanostructured (ns) materials exhibit many superior physical properties different from those of their conventional polycrystalline counterparts. These unique properties are frequently attributed to the significant increase in grain boundary density due to the small grain size. Over the years the research on ns materials has mainly focused on grain boundaries, whereas for the other component, nanocrystallites, the work is still very limited. In general, it is suggested that the crystalline component remains a perfect structure and has no significant influence on the unusual properties. However, a series of investigations on various ns materials synthesized by different techniques shows that the structural characteristics of nanocrystallites may evidently deviate from those of perfect crystals [1–11]. Quantitative x-ray diffraction (XRD) measurements for ns body-centred cubic (bcc) and face-centred cubic (fcc) metals (Fe, Nb, Cr, Ni, Pd and Cu) show that, with a reduction in grain size, the lattice parameters of nanocrystallites are slightly increased (mostly less than 1%) with respect to the ideal lattice constants [1–7]. Similar phenomena have also been reported in ns trigonal and body-centred trigonal (bct) samples (Se, Ni₃P and Fe₂B) [7–9]. On the other hand, the reverse experimental results, lattice contraction, are also found by different authors [10, 11]. So

far, many investigations on the crystal lattice structure of ns materials have yielded rather controversial results. Although the intrinsic reason is still unclear, it is believed that such an effect will certainly affect the physical properties of ns materials. At present, a quantitative estimation of the effect of the crystalline component on the unusual physical properties of ns materials is difficult, because a rational relationship describing the grain-size dependence of crystal lattice structure is not available yet. In this paper, a model for the variation of crystal lattice structure in ns materials will be developed and its effect on the unusual physical properties will be discussed.

2. Crystal lattice distortion of ns materials

2.1. Effects of interface tension

For a conventional polycrystalline material, the interface compression stress arising from interface tension is negligible. However, for a polycrystalline material with a nanometre-scale microstructure, interface stresses can no longer be neglected because, according to surface thermodynamic theory, the compression stress induced by interface tension is on the order of γ/L , where γ and L denote the interface tension coefficient and the grain size, respectively [12]. The internal pressure on crystal structure will lead to a lattice contraction. For crystallites with cubic lattice structure, the lattice contraction ($\overline{\Delta r_1}$), due to interface tension, is given by [13]

$$\overline{\Delta r_1} = -\frac{4}{3} \frac{\gamma k a_0}{L} \quad (1)$$

where k is the compressibility of the material and a_0 is the nearest-neighbour atom distance of a perfect lattice.

2.2. Effect of stress field induced by excess volume in grain boundaries

Owing to the relatively disordered arrangement of atoms at grain boundaries of ns materials, the grain boundaries inherently contain a certain amount of excess volume in the form of vacancies and vacancy clusters. These defects will induce a stress field and make the atoms in crystallites move from their normal lattice sites. Our previous model [14], based on a nonlinear elasticity theory, can describe how this stress field affect the crystal lattice structure, which was used by different authors to explain the experimental results [2, 13, 15–17]. Since there are some errors in the previous work, a modified model is given in this paper. For simplicity, a nanometre-sized polycrystal model is depicted schematically in figure 1. According to the elasticity theory [18], the deviation of atoms near vacancies/vacancy clusters from their normal sites obeys a $1/x^2$ law, in which x is the distance from the atoms to the centre of the defects. If we consider the stress fields from the left and the right grain boundaries, the deviation of an atom in a crystallite from its ideal position ($\delta(x)$) is given by $\delta(x) = A[1/x^2 - 1/(L + \xi - x)^2]$, where ξ is the grain-boundary thickness and A is a correlation coefficient. The relative displacement of two adjacent atoms in a crystallite (Δr_2), resulting from the stress field from the grain boundaries, may therefore be approximated to

$$\Delta r_2 = \delta(x) - \delta(x + a_0) = A \left[\frac{1}{x^2} - \frac{1}{(L + \xi - x)^2} - \left(\frac{1}{(x + a_0)^2} - \frac{1}{[L + \xi - (x + a_0)]^2} \right) \right]. \quad (2)$$

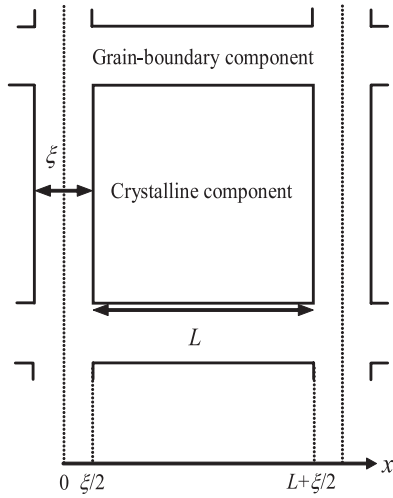


Figure 1. A nanometre-sized polycrystal model consisting of square-shaped crystallites with an orthogonal systems of grain boundaries.

A may be written as [14]

$$A = \frac{1}{16} \left[\frac{\xi^2(\xi + 2a_0)^2}{\xi + a_0} \right] (\sqrt[3]{1 + \Delta V_g} - 1) \quad (3)$$

where ΔV_g is the excess volume of grain boundaries, which is defined as $\Delta V_g = (V_g - V_0)/V_0$, where V_g and V_0 are the molar volumes of grain boundaries and perfect crystallites, respectively. The mean magnitude of the Δr_2 over the entire crystallite ($\overline{\Delta r_2}$) can be calculated:

$$\begin{aligned} \overline{\Delta r_2} &= \frac{1}{16(L - a_0)} \left[\frac{\xi^2(\xi + 2a_0)^2}{\xi + a_0} \right] (\sqrt[3]{1 + \Delta V_g} - 1) \int_{\xi/2}^{L + \xi/2 - a_0} \left[\frac{1}{x^2} - \frac{1}{(L + \xi - x)^2} \right. \\ &\quad \left. - \frac{1}{(x + a_0)^2} + \frac{1}{[L + \xi - (x + a_0)]^2} \right] dx \\ &= \frac{a_0}{2(L - a_0)} \left[\frac{\xi(\xi + 2a_0)}{\xi + a_0} - \frac{\xi^2(\xi + 2a_0)^2}{(\xi + a_0)(2L + \xi)(2L + \xi - 2a_0)} \right] \\ &\quad \times (\sqrt[3]{1 + \Delta V_g} - 1). \end{aligned} \quad (4)$$

Generally, the second term in the square bracket of equation (4) is smaller than the first term, indicating that the stress field induced by the excess volume in the grain boundaries results in lattice expansion. It is worth mentioning that the upper limit of the integral in equation (4) is $L + \xi/2 - a_0$, rather than $L + \xi/2$. This is because, when $x = L + \xi/2$, equation (2) refers to the relative displacement of two atoms in the positions of $L + \xi/2$ and $L + \xi/2 + a_0$. However, the atom at the position $L + \xi/2 + a_0$, in fact, exists in the grain boundary.

2.3. Total crystal lattice distortion

Combining equations (1) and (4), we may obtain the total deviation of the nearest-neighbour atom distance from the perfect distance in the crystalline component (Δr_c):

$$\begin{aligned} \Delta r_c = \overline{\Delta r_2} + \overline{\Delta r_1} &= \frac{a_0}{2(L - a_0)} \left[\frac{\xi(\xi + 2a_0)}{\xi + a_0} - \frac{\xi^2(\xi + 2a_0)^2}{(\xi + a_0)(2L + \xi)(2L + \xi - 2a_0)} \right] \\ &\quad \times (\sqrt[3]{1 + \Delta V_g} - 1) - \frac{4}{3} \frac{\gamma k a_0}{L}. \end{aligned} \quad (5)$$

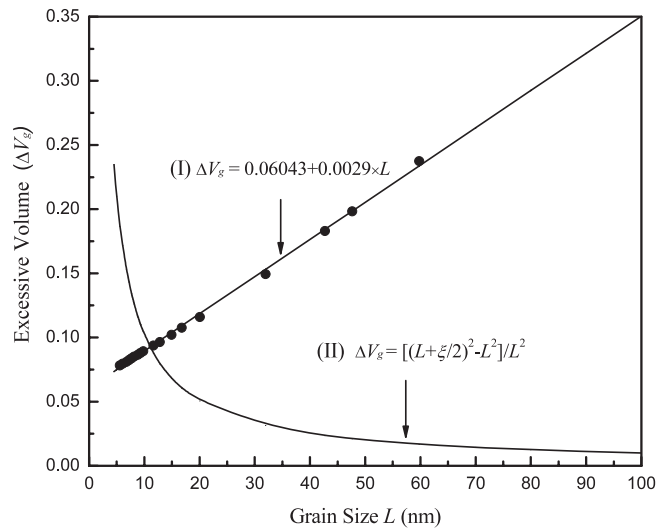


Figure 2. Changes of the excess volume of grain boundaries ΔV_g with grain size L in ns materials prepared using the as-crystallized method (I) [19] and as-milled method (II) [20]. (The relationship in I is obtained by fitting the experimental data of Lu *et al* [19]. The curve II corresponds to $\xi = 1$ nm).

Experimental results show that ΔV_g is a function of the grain size, and depends on the preparation methods. For ns materials prepared by crystallization from the amorphous state, the ΔV_g increases with increasing grain size, as shown by curve I in figure 2 [19], whereas for the ns materials prepared by ball milling, the ΔV_g exhibit a completely different dependence on grain size, as shown by curve II [20]. By taking $a_0 = 0.25$ nm, $\gamma = 0.21$ N m⁻¹ [21], $k = 6.0 \times 10^{-12}$ Pa⁻¹ [22] and assuming $\xi = 1$ and 2 nm, respectively, the theoretical Δr_c is calculated and the results are plotted in figure 3. Currently available experimental data are also plotted in the same figure for comparison. It is seen that the theoretical results may well account for the experimental observations. In addition, the present results show that the crystal lattice structure is strongly dependent on the grain-boundary structure of ns samples. Since the grain-boundary structure is different for samples prepared by different methods and/or conditions, this may explain why different authors frequently observe different experimental data, even for ns samples with the same grain size and composition.

The interface tension coefficient (γ) in equation (5) is an important parameter in determining the role of the compression term in Δr_c . This parameter depends on the interface structure between the crystalline component and the grain-boundary component. For free particles with very small size, the internal pressure induced by the surface is certainly important. Lu and Zhao pointed out that, for ns materials that are not fully dense, the porosity of the grain boundaries will lead to an increase in crystallite surface area and therefore the effects of surface tension on the crystal lattice could become very important, which may result in lattice contraction [7]. However, for fully dense ns materials, the nanocrystallites are embedded in a grain-boundary ‘phase’ matrix and there is a transition between crystallites and grain boundaries, as observed by high-resolution electron microscopy [23]. Thus, when the grain size is extremely small, some effect of hydrostatic compression would be expected inside the crystallites of ns materials, but this will be much weaker than the compression experienced inside isolated nanoparticles of the same size where the effect comes from the free surface energy, which is larger than the interface energy. For most cases, the $\overline{\Delta r_2}$ will be dominant in

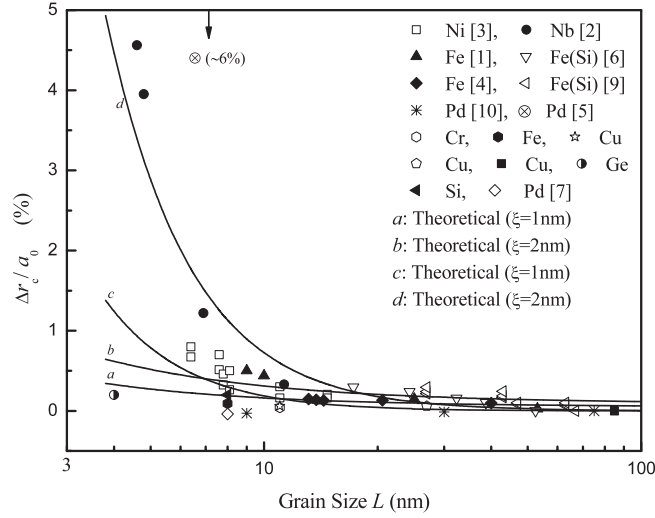


Figure 3. Theoretical $\Delta r_c/a_0$ versus L curves of ns materials compared with experimental data (a and b: as-crystallized; c and d: as-milled).

Δr_c . Some experimental results of lattice contraction are more likely attributed to macroscopic residual stresses in samples, as suggested by Sevillano [11]. So far, lattice contraction is often reported in ns samples synthesized by means of the consolidation of ultrafine powders or quenching [10, 11]. It is inevitable that there is a macroscopic residual compressive stress in these materials. In addition, it is known that dislocations may cause an increase in the volume of the material [24]. Experimental results show that dislocations are seldom present in nanocrystallites, because there is a strong stress field from the grain boundaries that tends to pull mobile dislocations out of the crystallites [23, 25]. Therefore, for nanometre-scale crystallites the lattice dislocations might hardly have a significant influence on the lattice structure.

3. Effects of lattice distortion on physical properties

The change in lattice structure is intrinsically related to the observed physical property variation. The thermal expansion coefficient (α_L) is taken as an example for analysis in this paper. The work of Wagner shows that the thermal properties of ns materials may be calculated by means of a quasi-harmonic Debye approximation (QDA), which is described in detail in [26]. According to QDA, α_L is a function of the nearest-neighbour atom distance. The nearest-neighbour atom distance in the crystalline component (r_c) is given by

$$r_c = a_0 + \Delta r_c = a_0 + \frac{a_0}{2(L - a_0)} \left[\frac{\xi(\xi + 2a_0)}{\xi + a_0} - \frac{\xi^2(\xi + 2a_0)^2}{(\xi + a_0)(2L + \xi)(2L + \xi - 2a_0)} \right] \times (\sqrt[3]{1 + \Delta V_g} - 1) - \frac{4}{3} \frac{\gamma k a_0}{L}. \quad (6)$$

Owing to the presence of excess volume, the nearest-neighbour atom distance in grain boundaries (r_g) is expressed as [26, 27]

$$r_g = a_0(1 + \Delta V_g)^{1/3}. \quad (7)$$

We consider a pure nickel system and use the following set of parameters $D = 11.8 \times 10^{-20}$ J/atom, $b = 1.35 \times 10^{10}$ m⁻¹, $a_0 = 2.5 \times 10^{-10}$ m and $\Theta_0 = 450$ K [27]. The

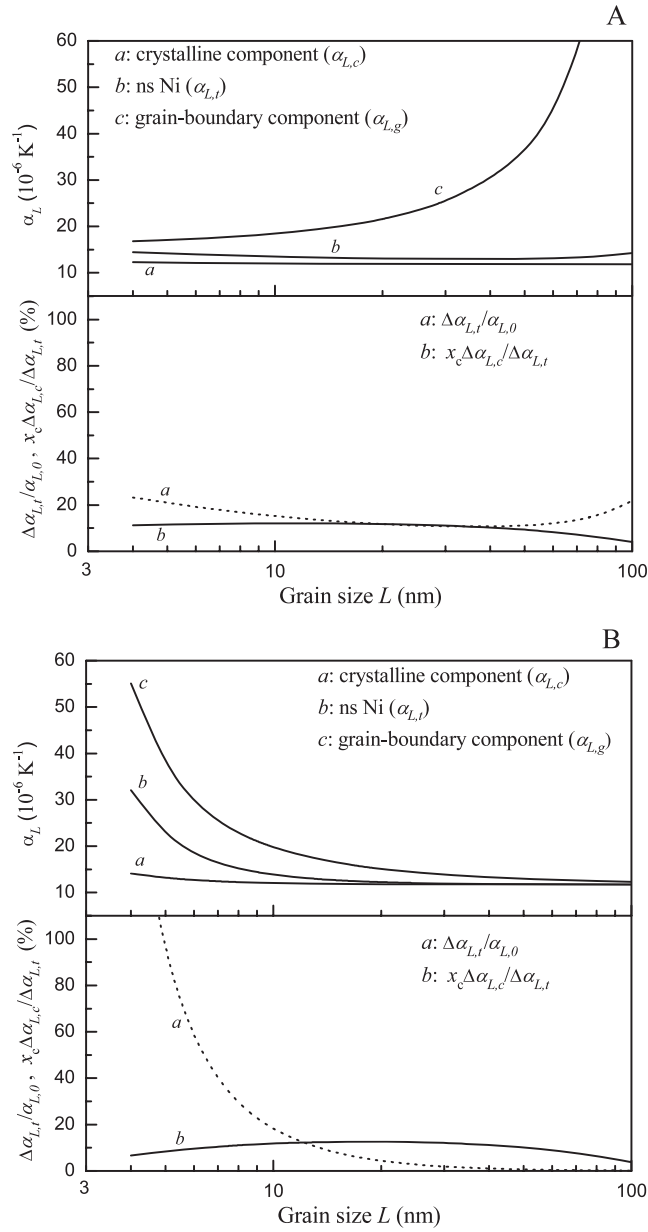


Figure 4. Variations in thermal expansion coefficients ($\alpha_{L,c}$, $\alpha_{L,g}$ and $\alpha_{L,t}$), the increase in thermal expansion coefficient ($\Delta\alpha_{L,i}/\alpha_{L,0}$) and the crystalline contribution to the increase in the thermal expansion coefficient ($x_c\Delta\alpha_{L,c}/\Delta\alpha_{L,t}$) as a function of grain size at $\xi = 1$ nm and $T = 300$ K ((A) as-crystallized; (B) as-milled).

thermal expansion coefficients in the crystalline component ($\alpha_{L,c}$) and the grain-boundary component ($\alpha_{L,g}$) may be calculated using QDA, respectively. The $\Delta\alpha_{L,i}$ ($\Delta\alpha_{L,i} = \alpha_{L,i} - \alpha_{L,0}$, $i = c$ and g) represent the deviation in the thermal expansion coefficient from the coarse-grained state ($r_c = a_0$). Since ns materials can be considered as a two-component system

with a crystalline component and a grain-boundary component, the change in the total thermal expansion coefficient ($\Delta\alpha_{L,t}$) of ns materials is given by [28]

$$\Delta\alpha_{L,t} = x_c\Delta\alpha_{L,c} + (1 - x_c)\Delta\alpha_{L,g} \quad (8)$$

where x_c is the atomic fraction of the crystalline component. Considering the nanometre-sized polycrystal model depicted in figure 1, x_c may be expressed as

$$x_c = \frac{L^3\rho_c}{[(L + \xi)^3 - L^3]\rho_g + L^3\rho_c} = \frac{L^3}{[(L + \xi)^3 - L^3](r_c^3/r_g^3) + L^3} \quad (9)$$

where ρ_g and ρ_c are the densities of the grain boundaries and crystallites, respectively. The calculated results are shown in figure 4. It is seen that the increase in the total thermal expansion coefficient relative to the coarse-grained counterpart ($\Delta\alpha_{L,t}/\alpha_{L,0}$) depends strongly on the preparation method. The $\Delta\alpha_{L,t}/\alpha_{L,0}$ of as-milled ns materials is much larger than that of as-crystallized ns materials when the grain size is extremely small, whereas for large grain size, the reverse is the case. Such a result can be attributed to the different grain-size dependence of the ΔV_g in the as-milled and as-crystallized ns states. In addition, figure 4 shows that the contribution of the crystalline component to the increase in the total thermal expansion coefficient ($x_c\Delta\alpha_{L,c}/\Delta\alpha_{L,t}$) is about 10% in a large grain-size range, which does not seem to be related obviously to the preparation method. Two reasons might be responsible for this. (1) For a given grain size and grain-boundary thickness (approximately a given x_c), the larger excess volume in the grain boundaries will cause a larger crystal expansion, as indicated in the last section. That is to say, if the $\Delta\alpha_{L,g}$ increases, the $\Delta\alpha_{L,c}$ also correspondingly increases, and consequently the $\Delta\alpha_{L,t}$ will become larger. This means that there is a positive correlation between the $\Delta\alpha_{L,c}$ and the $\Delta\alpha_{L,t}$ in ns materials, no matter which preparation method is used, as a result of which the value of $x_c\Delta\alpha_{L,c}/\Delta\alpha_{L,t}$ has no large difference for different methods. (2) The increase in grain size will reduce the crystal lattice distortion (i.e. reduce $\Delta\alpha_{L,c}$) but increase x_c . Therefore, for large grain size, the crystalline contribution to $\Delta\alpha_{L,t}$ may not yet be neglected. These results show that the unusual physical properties of ns materials are attributed not only to the grain boundaries but to crystallites as well. Similar theoretical analyses may also extend to other physical quantities. The present works make it possible to evaluate the effects of crystalline component on the unusual physical properties of ns materials in a large grain-size range.

4. Conclusions

Based on the surface thermodynamic theory and the elasticity theory, a model describing the grain-size dependence of the crystal lattice distortion of ns materials is developed. The interface tension and the stress field induced by the excess volume in grain boundaries are the main reasons for the deviation of the crystal lattice structure from the perfect structure. The effect of the crystalline component on the increase in the thermal expansion coefficient of ns materials is estimated using QDA, which indicates that, in addition to the grain boundaries, the crystalline component also has a contribution to the unusual physical properties.

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