The Linear Thermal Expansion of Bulk Nanocrystalline Ingot Iron from Liquid Nitrogen to 300 K

S. G. Wang · Y. Mei · K. Long · Z. D. Zhang

Abstract The linear thermal expansions (LTE) of bulk nanocrystalline ingot iron (BNII) at six directions on rolling plane and conventional polycrystalline ingot iron (CPII) at one direction were measured from liquid nitrogen temperature to 300 K. Although the volume fraction of grain boundary and residual strain of BNII are larger than those of CPII, LTE of BNII at the six measurement directions were less than those of CPII. This phenomenon could be explained with Morse potential function and the crystalline structure of metals. Our LTE results ruled out that the grain boundary and residual strain of BNII did much contribution to its thermal expansion. The higher interaction potential energy of atoms, the less partial derivative of interaction potential energy with respect to temperature $T$ and the porosity free at the grain boundary of BNII resulted in less LTE in comparison with CPII from liquid nitrogen temperature to 300 K. The higher LTE of many bulk nanocrystalline materials resulted from the porosity at their grain boundaries. However, many authors attributed the higher LTE of many nanocrystalline metal materials to their higher volume fraction of grain boundaries.

Keywords Linear thermal expansion · Bulk nanocrystalline materials · Severe rolling technique

Introduction

The thermal properties of materials are important parameters for material applications and they are associated with other physical and chemical properties. Thermal expansion of materials are very complicated processes, which comes from more than one contribution, such as electronic contribution, magnetism, and lattice contribution, etc. There can be no thermal expansion for harmonic approximation, the atoms vibrate about their equilibrium positions symmetrically whatever be the amplitude. To account for thermal expansion, one has to take into account the anharmonicity of lattice vibration and quasi-harmonic approximation, which provides the convenient method for discussing the thermal expansion of materials at moderate temperature [1]. The detailed theoretical discussion of thermal expansion on this basis was given by Barron [2]. In order to obtain thermal expansion of materials, one measured the temperature dependence of lattice parameter by X-ray diffraction or neutron powder diffraction [3, 4]. The negative thermal expansion of materials is an interesting subject which has been extensively investigated, many factors can cause negative thermal of materials, such as discontinuous and anisotropic thermal lattice vibrations [5, 6], the phase transition [7], the materials structures which can be characterized with rigid unit modes involving the local vibrational motion [8], the anisotropic thermal expansion to the saddle point van Hove singularity near the Fermi level [9].

Nanocrystalline (NC) materials have attracted considerable interests for their unusual physical, chemical, and mechanical properties. The thermal expansion of many NC materials has been investigated. The linear thermal expansion (LTE) of NC copper was nearly twice larger than that of its conventional coarse-grained polycrystalline
counterparts [10]. LTE of NC Ni–P alloy and the volume expansion of NC Se synthesised by crystallization of amorphous were 51 and 61% higher than those of their conventional coarse-grained polycrystalline counterparts, respectively [11, 12]. The thermal expansion of NC titanium powder compacts prepared by high-energy attrition milling was about 36% higher than that of titanium powder compacts [13]. NC Cr [14], Pb [15], and Au [16] of Debye–Waller parameters increased with decreasing grain size due to the increased concentration of defects in grain boundary with decreasing grain size. The increment of Debye–Waller parameters for these NC materials means that the thermal expansion of these NC materials increases with decreasing grain sizes. The thermal expansion of NC Cu prepared by magnetron sputtering increased with the increment of residual strain, which may be attributed to the density change of grain boundary defects/dislocations [17].

From above work on thermal expansion of NC materials, they own enhanced thermal expansion in comparison with their conventional polycrystalline counterparts. Many authors attributed the higher thermal expansion of NC materials to their metastable structure with the higher volume fraction of grain boundaries and higher concentration of defects/dislocations at grain boundaries [11–17]. However, in this work, we investigated LTE of bulk nanocrystalline ingot iron (BNII) at six directions on rolling surface and conventional polycrystalline ingot iron (CPII) at one direction, our LTE results of BNII are different from enhanced LTE of other NC materials. We explained qualitatively our LTE results with Morse potential function and microstructure of polycrystalline metals.

Experimental

Bulk nanocrystalline ingot iron was prepared by rolling CPII. The details of severe rolling technique were described in our previous report [18]. The microstructures of BNII were characterized with a Philips CM200 transmission electron microscope operated at 200 kV and X-ray diffraction (XRD). The microstructure of CPII was examined with XRD and optical microscopy. The measurement of LTE of BNII and CPII was carried out by strain gage method (Measurement of Thermal Expansion Coefficient Using Strain Gages, Technical note, TN-513-1, pp 119–129 (2007), Vishay Intertechnology, Inc., Malvern, PA (USA), www.vishaymg.com). All samples of BNII and CPII for LTE measurement were 12 mm × 9 mm × 1 mm. LTE of BNII were measured at six directions with different angles at 0° (rolling direction), 30°, 45°, 60°, 75°, and 90° (vertical to rolling direction) against rolling direction on rolling surface, the detailed description of LTE measurement directions for BNII is shown in Fig. 1. LTE of CPII was measured only in one direction due to the isotropy of CPII microstructure. We measured the linear thermal expansion parameter \( \beta_l(T) \), it was defined as

\[
\beta_l(T) = \frac{L(T) - L(300)}{L(300)}
\]  

where \( L(T) \) and \( L(300) \) are the lengths of specimen at certain measurement direction at temperatures \( T \) and 300 K, respectively. Another thermal expansion parameter, the linear thermal expansion coefficient \( \eta_l(T) \), was defined as

\[
\eta_l(T) = \frac{1}{L(T)} \frac{dL(T)}{dT}
\]  

We characterized the linear thermal expansion of BNII and CPII with Eq. 1 rather than Eq. 2, because Eq. 1 can directly characterize thermal expansion or contraction of materials during temperature change. \( \eta_l(T) \) may cause unexpected error for measured data. For the same material, \( \beta_l(T) \) of Eq. 1 in one case was larger than that in another case, while \( \eta_l(T) \) of Eq. 2 in the former case may be less than that of the latter case [19]. We fitted LTE data of BNII and CPII with the following equation

\[
\beta_l(T) = A_0 + BT + CT^2 + DT^3
\]  

at the temperature above \( \Theta_D / 20 \). \( \Theta_D \) is Debye temperature [1], and \( \Theta_D \) of iron is about 470 K [20]. \( \Theta_D / 20 \) is about 23.5 K for iron. Therefore, Eq. 1 is suitable for fitting our LTE results of BNII and CPII from liquid nitrogen temperature (77 K) to 300 K [1].
Results and Discussion

The transmission electron microscope image of BNII was shown in our previous work, the grain size of BNII varied from 50 to 89 nm with an equiaxed structure [18]. Figure 2 presents LTE of BNII at six measurement directions on rolling plane and CPII at one measurement direction from liquid nitrogen to 300 K. From Fig. 2, LTE of BNII at six measurement directions was less than that of CPII. For BNII, LTE at 30° was least LTE among LTE at the six measurement directions. Figure 2 indicates that BNII behaves the better stability of linear thermal expansion in comparison with CPII. Our LTE results of BNII are different from enhanced thermal expansion of other NC materials, although BNII also has the higher grain boundary volume fraction and higher concentration of defects at grain boundary. However, many authors thought that the two factors resulted in the enhanced thermal expansion for NC materials and that LTE of NC materials increased with decreasing grain sizes.

The measurement direction dependence of the parameters \(A_0\), \(B\), \(C\), and \(D\) of BNII and CPII are shown in Figs. 3, 4, and 5, can be obtained by fitting the data of LTE of BNII and CPII with Eq. 3. \(A_0\), \(C\), and \(D\) of BNII and CPII are negative values and \(B\) of BNII and CPII are positive values. Therefore, we can think that \(T^2\) term is associated with the power of thermal expansion for BNII and CPII, which origins from the energy that crystal lattice and conduction electrons absorb with the increment of temperature [1]. \(T\) and \(T^3\) terms are associated with the resistance of thermal expansion including the attractive forces among atoms, the collision of conduction electrons, the texture, and defects structure of materials, etc. According to Figs. 4 and 5, the contribution of \(T\) term to thermal expansion is larger than that of \(T^3\) term for BNII and CPII. The absolute value of \(A_0\) of CPII is less than those of BNII at the six measurement directions in line with Fig. 3, which means that the shrinkages of BNII at six measurement directions were larger than that of CPII when temperature \(T \rightarrow 0\). \(B\) of CPII is less than that of BNII at 90°, and is larger than those of BNII at the rest five measurement directions. \(C\) of CPII is less than those of BNII at all the measurement directions, which means that the power of thermal expansion was enhanced for BNII. \(D\) of CPII is less than that of BNII at 60°, and is larger than those of BNII at the rest five measurement directions. The attractive forces among atoms should contribute to thermal expansion as \(T\) term because \(B(\sim 10^{-6})\) is larger than \(D(\sim 10^{-11})\). We should need other further investigation and experiments if we intend to understand the effect of above each factor on thermal expansion as \(T\) or \(T^3\) term. This is an interesting and fundamental problem for thermal expansion. We will investigate this problem further in the future. We also should...
consider the magnetic contribution to thermal expansion for magnetic materials. Although the power of thermal expansion of BNII was enhanced in comparison with that of CPII in line with Fig. 4, the resistance of thermal expansion for BNII were also larger than that of CPII from Figs. 4 and 5 in the meantime. As the result of the competition between the power and resistance of thermal expansion, the actual thermal expansion of BNII was less than that of CPII from Fig. 2, which means that the power of thermal expansion is less than the resistance of thermal expansion for BNII. The power and resistance of thermal expansion depend on the variation of interaction potential energy among atoms with temperature.

In the view of physics nature, the thermal expansion of condensed materials was formed after the atoms absorbed energy and the distances between them became larger with temperature. The motion of atoms was determined by their interaction potential energy and their variation with temperature $T$. The larger interaction potential energy among atoms and the less its variation with temperature $T$, the more difficult the thermal expansion is. The interaction potential energy between the two atoms $i$ and $j$ for bulk materials could be characterized by Morse potential function $\phi(i, T)$ at temperature $T$ [21]

$$\phi^l(i, T) = A \left\{ e^{-2z(r_{ij}(T) - r_0)} - e^{-z(r_{ij}(T) - r_0)} \right\}$$  

(4)

where $z$ and $A$ are the constants with dimensions of reciprocal distance and energy, respectively, and $r_0$ is the equilibrium distance of approach of the two atoms, the three parameters depend on materials and their processes history, etc. $r_{ij}(T)$ is the distance between two atoms $i$ and $j$ at temperature $T$. We usually consider the interaction potential energy between the nearest neighbor atoms for metal materials. In fact, we should also consider the effect of the second neighbor atoms on interaction potential energy [22]. $\phi_{NANO}(i, T)$ and $\phi_{CPII}(i, T)$ stand for the total interaction potential energies of atom $i$ among its the nearest and second neighbor atoms of BNII and CPII at temperature $T$, respectively. $\phi_{NANO}^m(i, T)$ and $\phi_{CPII}^m(i, T)$ are the interaction potential energies between atom $i$ and the nearest neighbor atom $m$ for BNII and CPII, respectively. $\phi_{NANO}^{m_n}(i, T)$ and $\phi_{CPII}^{m_n}(i, T)$ are the interaction potential energies between atom $i$ and the second neighbor atom $n$ for BNII and CPII, respectively. $m$ and $n$ are 8 and 6 for metals with body-centered-cubic structure, respectively; $m$ and $n$ are 12 and 6 for metals with face-centered-cubic structure, respectively. We can obtain the following equation

$$\phi_{NANO}(i, T) > \phi_{CPII}(i, T)$$  

(5)

because BNII suffered from severe rolling and severe deformation processes can enhance the interaction potential energy among atoms, residual strain, and concentration of defects at grain boundary. It is well-known that the interaction potential energy among atoms should decrease with the increment of temperature, and then the interaction distance of atoms increased with temperature, so thermal expansion happened. We defined $f_{NANO}(i, T)$ and $f_{CPII}(i, T)$ as the first partial derivative of $\phi_{NANO}(i, T)$ and $\phi_{CPII}(i, T)$ with respect to temperature $T$ for BNII and CPII, respectively

$$f_{NANO}(i, T) = \frac{\partial \phi_{NANO}(i, T)}{\partial T}$$  

(6)

$$f_{CPII}(i, T) = \frac{\partial \phi_{CPII}(i, T)}{\partial T}$$  

(7)

In fact, linear thermal expansion depends on interaction potential energy, the first partial derivative of interaction potential energy with respect to temperature $T$ and $\gamma$, the linear density of atoms at certain measurement direction. $\gamma$ depends on crystal structure of metals (such as face-centered-cubic and body-centered-cubic structure, etc.) and the measurement direction. The larger $\phi(i, T)$ and the less $f(i, T)$, the less thermal expansion is; the larger the linear density of atoms, the larger linear thermal expansion is. Therefore, we can give the following Eq. 8 from Fig. 2

$$f_{NANO}(i, T) \leq f_{CPII}(i, T)$$  

(8)

The values of $f_{NANO}(i, T)$ and $f_{CPII}(i, T)$ depend on the three parameters $B$, $C$, and $D$ of BNII and CPII. According to the physical nature of linear thermal expansion and above discussion, we can obtain the following equation

$$\beta_i(T) \propto ||f(i, T)||^\gamma$$  

(9)

where $t$ is a constant. We can explain qualitatively the results of LTE for BNII and CPII: (1) LTE of BNII at six
measurement directions were less than those of CPII because \( \phi_{\text{NANO}}(i, T) \) was larger than \( \phi_{\text{CPII}}(i, T) \) and \( f_{\text{NANO}}(i, T) \) was less than \( f_{\text{CPII}}(i, T) \); (2) LET of BNII depend on measurement direction because \( \gamma \) depends on crystal structure and measurement direction. The rolling surface was combined with several crystalline planes from X-ray diffraction of BNII and CPI at room temperature as shown as Fig. 6 [18], the atoms at certain measurement direction come from different crystalline planes, \( \gamma \) is difficult to be calculated for polycrystalline metals. It is also difficult to determine the interaction potential energy among atoms and its variation with temperature, they are associated with many factors, such as kinds of atoms, the microstructure of materials, heat treatment history, and rolling history, etc. Therefore, it is difficult to analyze quantitatively linear thermal expansion and there is a paucity of theoretical work on the thermal expansion of anisotropic materials. A lot of theoretical problem on thermal expansion should be investigated further in the future.

LTE of polycrystalline metal materials can be described by two-component system, the crystallite component and grain boundary component [23]. It is well-known that the thermal expansion of coarse-grained polycrystalline materials comes from crystallite and grain boundary, and that grain boundary has less contribution to the thermal expansion because of their very little fraction volume in the view of materials science. Many authors thought that LTE of many bulk NC materials were higher those of their conventional coarse polycrystalline counterparts due to the higher volume fraction of NC materials grain boundaries and concentration of defects at grain boundaries [10–17]. It is normally considered that the thermal expansion of grain boundary was enhanced in comparison with that of crystallite due to their excess volume for bulk NC materials [15, 23]. However, the grain boundary of BNII did less contribution to thermal expansion because LTE of BNII at six measurement directions were less than those of CPII from liquid nitrogen to 300 K according to Fig. 2. It was suggested that the relatively large changes of the thermal expansion previously reported may be due to porosity rather than the small grain size [23]. The thermal expansion of porosity is larger than that of atom in crystallite and grain boundary during the increment of temperature, which can cause enhanced thermal expansion for many bulk NC materials. The pressure of porosity increases with the decrement of grain sizes and increment of temperature. The grain boundary of BNII can not exist porosity because BNII maintained bulk state all the time during severe rolling process, it is impossible that porosity could be introduced during severe rolling processes, and the grain boundary of BNII can not be polluted by porosity or other atoms.

LTE of polycrystalline materials can be described by two-component system as following equation [24]

\[
\alpha_i = F_{\text{GBs}}\alpha_{i}^{\text{GBs}} + (1 - F_{\text{GBs}})\alpha_{i}^{c} \tag{10}
\]

where, \( \alpha_i \), \( \alpha_{i}^{\text{GBs}} \), and \( \alpha_{i}^{c} \) are LTE of bulk, grain boundary, and crystalline, respectively. \( F_{\text{GBs}} \) is the volume fraction of grain boundary,

\[
F_{\text{GBs}} = \frac{3\delta}{d} \tag{11}
\]

where \( \delta \) and \( d \) are constants relative to the grain boundary thickness and grain size, respectively. The ratios of \( \alpha_{i}^{\text{GBs}}/\alpha_{i}^{c} \) were between 1.2 and 12.7 for NC Ni–P alloy with different grain sizes [11], and 2.5–5.0 for other NC materials [15, 25]. According to Fig. 2, the thermal expansion of BNII mainly come from the contribution of crystallite because LTE of BNII are less than those of CPII. From Fig. 2, the crystal lattice parameters of BNII grew at slower velocity in comparison with those of CPII from liquid nitrogen to 300 K. One can obtain volume expansion of materials with the data of lattice parameters at different temperature. However, linear thermal expansion of materials cannot be obtained with the data of lattice parameters except for single crystal materials because grain orientations of polycrystalline materials are very difficult to determine along the measurement direction [17]. We had to conclude that grain boundary of BNII do less contribution to its thermal expansion. Our LTE results of BNII and CPII were very different from enhanced thermal expansion for other NC materials compared to their conventional polycrystalline counterparts [10–16] and negative thermal expansion of materials [5–9]. However, as shown as Fig. 2, \( \beta(T) \) of BNII are less than those of CPII, although BNII has higher volume fraction of grain boundary and residual strain as shown our previous work [18]. The better stability of linear thermal expansion of BNII, the higher tensile strain as shown our previous work [18].
strength [26], enhanced wear and corrosion resistance of BNII, and enhanced corrosion resistance of bulk nanocrystalline stainless steel 304 [18, 27–29] in comparison with those of their conventional polycrystalline counterparts. Therefore, BNII and bulk nanocrystalline 304 stainless steel prepared by severe rolling technique are potential to be applied in many fields. Severe rolling technique for bulk nanocrystalline metal materials can improve several properties in comparison with their conventional coarse polycrystalline counterparts at the same time rather than improve certain property at cost of another property. This is the advantage and feature different from other preparation techniques for bulk nanocrystalline metal materials.

Residual strain exists in BNII because BNII was suffered from severe rolling during preparation processes [18]. However, LTE of BNII at six measurement directions were less than those of CPII from liquid nitrogen temperature to 300 K, which indicates that the residual strain of BNII did not contribute to the LTE of BNII. In fact, the residual strain can increase interaction potential energy among atoms, and then they were eliminated gradually with temperature. Therefore, residual strain can make thermal expansion slow down. In fact, residual strain can increase the pressure of porosity at grain boundary, which can result in the higher LTE of many NC materials in comparison with their conventional polycrystalline counterparts because porosity at grain boundary usually expanded more quickly compared to metal atoms at crystallite and crystallite boundary. So it is easy to understand the fact that the thermal expansion of some NC materials increased with residual strain, and that the reason why LTE of many other bulk NC materials were higher than their conventional coarse polycrystalline counterparts, and that many authors attributed the higher thermal expansion of NC materials to their higher volume fraction of grain boundary and residual strain [11, 13, 17, 30].

It was suggested that the relatively large changes of thermal expansion previously reported may be due to porosity or impurity at grain boundary rather than the small grain size [31]. Our experimental results in linear thermal expansion support this point of view. It is normally considered that the grain boundary have an enhanced thermal expansion in comparison with that of crystallite due to their excess volume [21]. Many preparation techniques, such as inert gas condensation, ball-milling, and magnetron-sputtering, changed the state of materials, such as bulk → powder → bulk or thin film and powder → bulk during nanocrystallization processes. Many NC materials have a considerable amount of entrained porosity, which was introduced during nanocrystallization processes. The porosity in NC materials may drastically alter results for the thermal expansion and, therefore, impair measurement reliability and accuracy. In fact, the thermal expansions of NC materials were found to be sensitive to the mode of preparation and their consequent time–temperature history [17, 30–32]. However, the densities, state and compositions of NC materials by severe rolling technique were not changed and their microstructures of grain boundary were continuously changed with porosity free at grain boundary during the whole preparation processes. This is the reason why the grain boundary did less contribution to the thermal expansion of BNII.

**Conclusion**

Bulk nanocrystalline ingot iron had less linear thermal expansion in comparison with conventional polycrystalline ingot iron from liquid nitrogen temperature to 300 K. The thermal expansion depends on the interaction potential energy of atoms and the first partial derivative of it with respect to temperature, grain boundary structure, and residual strain, etc. Different preparation techniques of bulk nanocrystalline metal materials can result in different microstructures associated with thermal expansion. We can rule out the larger contribution of grain boundary and residual strain to linear thermal expansion for BNII. The porosity free at BNII grain boundary results in the less contribution of higher volume fraction and residual strain to thermal expansion of BNII. Linear thermal expansion of many NC materials was higher than those of their conventional coarse polycrystalline counterparts because the expansion velocity of the porosity at the grain boundary is larger than the expansion velocity of atoms inside crystallite and at grain boundary.

**Acknowledgments** Authors are grateful to the financial support of Natural Sciences of Foundation of China, Contract No.: 50501023, 50771098 and the National Major Fundamental Research Program (No. 2010CB934603) of China, Ministry of Science and Technology China.

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