Theoretical and experimental study of the thermal expansion coefficient of the Ni$_3$Al alloy

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Abstract. The classical and $ab$ initio molecular dynamic (MD) simulation of the thermal expansion coefficient of the Ni$_3$Al alloy has been performed in the temperature interval 300 - 1500 K with the increment $\Delta T = 100$ K. The obtained results are compared with the experiment. It is found the classical MD overestimate and the $ab$ initio MD underestimate the experimental results. The results of $ab$ initio simulation is more close to the experiment without any adjustable parameters but it is very timeconsuming.

1. Introduction
Theoretical and computational modeling is becoming increasingly important in the development of advanced high performance materials for industrial applications. Atomic level understanding of the properties of fcc transition metals and it alloys under various conditions is important in the technological application. The nickel-based alloys play an important role in terms of their unique combination of properties. The Ni$_3$Al alloys are being developed as a new class of high-temperature structure materials. In last years the L1$_1$ Ni$_3$Al compound has been the subject of extensive investigation both the experimental and theoretical methods [19]. One of the important physical properties as the thermal expansion coefficient (TEC) is the subject of our study.

2. Thermal expansion coefficient
Most materials are subject to thermal expansion: a tendency to expand when heated, and to contract when cooled. Solids typically expand to heating and contract to cooling. This response to temperature change is expressed as its coefficient of thermal expansion (CTE) or simply thermal expansion coefficient (TEC). The coefficient of thermal expansion is used in two ways: as a volumetric thermal expansion coefficient $\beta$, as a linear thermal expansion coefficient $\alpha$ [1]:

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p,$$
$$\alpha = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_p,$$

where $T$ is the temperature, $V$ is the volume, derivative is taken at constant pressure $p$; $\beta$ measures the fractional change in volume as temperature increases at constant pressure.
Table 1. Parameter sets for Sutton-Chen many-body potential for Al and Ni [5]

|   | n  | m  | ε (eV) | c    | a (Å) |
|---|----|----|--------|------|-------|
| Al| 7  | 6  | 0.033147 | 16.399 | 4.05  |
| Ni| 9  | 6  | 0.015707 | 39.432 | 3.52  |

The linear thermal expansion coefficient relates the change in temperature to the change in a material’s linear dimensions. It is the fractional change in length of a bar per degree of temperature change. The volumetric thermal expansion coefficient can be measured for all substances of condensed matter (liquids and solid state). The linear thermal expansion can only be measured in the solid state and is common in engineering applications. For exactly isotropic materials, the linear thermal expansion coefficient is very closely approximated as one-third the volumetric coefficient: \( \beta \cong 3\alpha \). The expansion of a crystalline material occurs only when the force field of the crystal deviates from a perfect quadratic. If the force field is perfectly parabolic, no expansion will occur. The MD is the good tool in this sense for TEC simulation, because it usually includes the anharmonic effects.

3. Simulation Methods and results

We use the two popular simulation methods in our computer experiment: i.e. the classical molecular dynamics (MD) [2] and the ab initio molecular dynamics (AIMD) [3]. The DL_POLY package [4] is one of the best realization of the first one and the SIESTA package [8] is the second one. There are some advantages and and drawbacks in of the methods. The classical MD gives good statistics, however the problem of choice of the interatomic potential with some adjustable parameters is the main problem of it. The AIMD is the modern, universal and powerful simulation method. It gives good results without any adjustable parameters, but it is very timeconsuming. For this reason the number of atoms in simulation system are rarely exceeds 100 in AIMD. However, the combination of this two methods permit us use all the advantages both of it and obtain good results for a real complicated systems.

We used the many-body Sutton-Chen (SC) interatomic potential in DL_POLY calculations. SC potential was specially created for describing interatomic interaction forces of transition metals and at present, it is one of the most frequently used for modeling metal systems. Total potential energy of the pure metals and alloys in Sutton-Chen formalism for the system of \( N \) atoms is given as follows [5, 6, 7]:

\[
U_{tot} = \sum_{i}^{N} U_i = \sum_{i}^{N} \left\{ \sum_{j \neq i}^{N} \frac{1}{2} \varepsilon_{ij} \left( \frac{a_{ij}}{r_{ij}} \right)^{m_{ij}} - c_i \varepsilon_{ii} \left[ \sum_{j \neq i}^{N} \left( \frac{a_{ij}}{r_{ij}} \right)^{m_{ij}} \right]^{1/2} \right\}, \tag{1}
\]

The first term in Eq. (1) is two body repulsive interaction between the atoms \( i \) and \( j \), separated by a distance \( r_{ij} \). The second term represents the many-body cohesion term associated with atom \( i \). The square root term introduces a many-body component into the energy summation. The relatively simple analytical form of this potential explains it popularity for simulation of the metals and alloys. SC potential parameters for Al and Ni are given in Table 1. The adjustable potential parameters are fitted either from an experiment or from ab initio calculations. The temperature interval \( T = 300 \text{ K} - 1500 \text{ K} \) with the increment \( \Delta T = 100 \text{ K} \) was used for TEC calculation.
The ab initio Car-Parrinello molecular dynamics (AIMD) [3] in the framework of the density functional theory (DFT) [9, 10] has been used in the TEC calculations. The exchange-correlation term is described by the generalized gradient approximation (GGA) in the Beke-Lee-Yang-Parr (BLYP) implementation [11, 12]. Norm-conserving pseudopotentials [13] with s and p as nonlocal and d al local orbitals were used. The SIESTA code [8] were used in the AIMD calculation. The SIESTA package is based on flexible linear combination of atomic orbitals (LCAO) basis sets [14], with actual and efficient Order-N scaling [15]. The cutoff radius was equal 250-Ry, it is guarantee the convergence of the self-consistent procedure to less then 1 meV/atom. The maximum 25 electronic steps were used on the each ionic step in the atomic relaxation procedure. The Parinello-Rahman molecular dynamics [16] with variable shape and volume of the unit cell has been used (NPT ensemble). The fcc supercell with 32 atoms was used as the starting point in all SIESTA calculations. The temperature interval T = 300 K – 1500 K with the increment ∆ T =100 K was used in SIESTA calculation. All results both theoretical and experimental are shown on Fig. 1 and in Table 2. We see the classical MD overestimate and the AIMD underestimate the experimental TEC, but the AIMD results are more close to the experiment.

4. Experimental details
The compositions of the alloys studied are 74.5 at. % Ni, 24.5 at. % Al. The (001) single crystal was grown in vacuum furnace by the Bridgman technique with the growth rate of 1 mm/min and temperature gradient 80 grad/cm. Crystal was annealed at 1473 K for 6 h in vacuum. The growth structure and phase composition at room temperature were previously examined by metallography (EPYTip optical microscope), electron microscopy (JEM-200 ), neutron diffraction and described in detail in [17, 18]. The Ni3Al single crystal showed cellular-dendritic structure with small content (less than 1 vol. %) of β phase (NiAl) as result of directional solidification. Our study showed rather high level of its crystal structure perfection [18]. The total misorientation between the individual large blocks did not exceed 3°. The room temperature value of lattice parameter was a = 0.35705 nm.

At high temperatures, the alloys were investigated by the high-temperature -ray diffraction method in the β radiation using the (004) reflection on DRON-3 diffractometer with UVD-2000 device. The experiment was carried out in vacuum of 2 · 10−4 mmHg and included the heating of single-crystal specimens (100) plates 3 mm thick) at rate of 5 grad/min in the range from 1173 K to 1473 K in steps of 50 . Prior t recording the -ray diffraction patterns, fine adjustment was performed to obtain the reflection from only one large block (according to the θ − 2θ scheme). The temperature was measured by W-R thermocouple directly contacting the specimen.

Since thermal expansion coefficient (TEC) α somewhat increases with temperature, it was
Table 2. Theoretical and experimental TEC in $10^{-5}K^{-1}$.

| Temp. (K) | DL POLY | Exper. | SIESTA |
|-----------|---------|--------|--------|
| 300 - 1200 | 2.0257  | 1.51±0.04 | 1.4110 |
| 1200 - 1400 | 2.6138  | 1.91±0.04 | 1.8148 |

determined in two temperature ranges: $\alpha = (1.51 \pm 0.04) \cdot 10^{-5}K^{-1}$ at the interval from 290 to 1273 K and $\alpha = (1.91 \pm 0.04) \cdot 10^{-5}K^{-1}$ at the interval from 1273 to 1473 K. Stoloff [19] gives $\alpha = 1.51 \cdot 10^{-5}K^{-1}$ for 1073 K. Based on the data of [20], the for the Ni$_3$Al binary alloy can be estimated as $(1.54 \pm 0.04) \cdot 10^{-5}K^{-1}$ below 1273 K and $(2.03 \pm 0.04) \cdot 10^{-5}K^{-1}$ above 1273 K. These values are in good agreement with our results. Close value of the $(\alpha = 1.87 \cdot 10^{-5}K^{-1})$ at the range of 1273 - 1523 K was found by x-ray diffraction when studying the Ni$_3$Al-based phase in the superalloy of VKNA type (95% of the $\gamma'$ phase) [21].

5. Conclusions
The classical and $ab$ initio molecular dynamic simulation of the thermal expansion coefficient of the Ni$_3$Al alloy has been performed in the temperature interval 300 - 1500 K with the increment $\Delta T = 100$ K. The obtained results are compared with the experiment. It is found the classical MD overestimates and the $ab$ initio MD underestimates the experimental results. The results of $ab$ initio simulation is more close to the experiment without any adjustable parameters but it is very timeconsuming.

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